Deposition of Fines Entrained in Bitumen-derived Light Gas Oil on Hydrotreating Catalyst: Impact of Process Parameters

A Thesis Submitted

to the College of Graduate Studies and Research

in Partial Fulfilment of the Requirements

for the Degree of Master of Science

in the Department of Chemical and Biological Engineering

University of Saskatchewan

By

Rachita Rana

Saskatoon, Saskatchewan, Canada

Permission to Use

In presenting this thesis towards the partial fulfilment of the requirements for Master of Science Degree from the University of Saskatchewan, the author agrees that the libraries of the University of Saskatchewan may make it freely available for reference. The author further agrees that the copying of this thesis in any manner, entirely or partially, for academic purpose may be granted by the supervisors or other professors, or in their absence, by the Department of Chemical and Biological Engineering Head or by the Dean of the College of Graduate Studies and Research at the University of Saskatchewan. However, it is understood that any copying or publication or use of this thesis or parts thereof for financial gains shall not be permitted without the author's written approval. It is also understood that the author would be recognized and so will the University of Saskatchewan be for any scholarly use of any material available in this thesis.

Request for permission to copy or to make other use of the material herein as whole of part should be addressed to:

Head of the Department of Chemical and Biological Engineering

57 Campus Drive

University of Saskatchewan

Saskatoon, Saskatchewan, Canada

S7N 5A9

Abstract

In this work, the impact of hydrotreating process parameters on the deposition of fines that are present in bitumen-derived light gas oil was studied. NiMo/γAl_2O_3 catalyst was synthesized in the laboratory to run the hydrotreating experiments in a batch system. The process parameters studied were temperature (355, 365 and 375 °C) and pressure (1200, 1300 and 1400 psig). Additionally, different loadings of the fines (1, 1.25 and 1.5 g) in 200 ml of light gas oil were taken to understand the impact of variation in particle loading on their deposition. The study was conducted in two phases; the first phase involved kaolin as model fines and in the second phase asphaltene coated kaolin was synthesized and used as model fines. Most of the experiments reported were designed using statistical technique, ie. central composite design and hence the results account for reproducibility. Other experiments testing the individual parameters were repeated. In all cases the error for bed deposition was ±5% and for sulfur conversion was ±2%.

For kaolin suspended feed, temperature and particle loading had the most significant impact on particle deposition as individual parameters. High temperature (375 °C) led to more bed deposition and the trend was similar for particle loading in the feed. However, statistical analysis suggested that there was a combined effect of temperature and pressure on bed deposition. Bed deposition and sulfur conversion were optimized for a feed with varying particle loading (0.8-1.6 g). It was found that for a feed with high particle loading (1.6 g) the hydrotreating temperature should be 360 °C and the pressure should be 1450 psig. When the particle loading in 200 ml of feed was reduced to 0.8 g the optimized temperature for hydrotreating was 364 °C and the pressure was 1380 psig. In both optimizations the target bed deposition on the catalyst bed was taken close to the minimum (0.1 g) and the sulfur conversion was taken close to the maximum (60 wt%).

When asphaltene coated kaolin was taken as model fines, two different sized particles ranges (4-6 and 9-11 μm) were synthesized to study the impact of particle size on bed deposition. Maximum bed deposition and sulfur conversions were attained at 375 °C; however pressure did not show a clear impact for bed deposition. It was also found that smaller particles (4-6 μm) deposited more on the catalyst bed as compared to the large size particles. When asphaltene coated kaolin is used as model fines, there is a preferential deposition of the fines on the reactor assembly as opposed to kaolin where the deposition is more on the catalyst bed.

X-ray fluorescence (XRF) results suggest that in case of asphaltene coated kaolin, the fines settle at the bottom of the catalyst bed causing deep-bed filtration. The optimization results show that higher pressure (1300 psig), lower temperature (365 °C) would lead to less bed deposition without affecting the sulfur conversion of the feed.

Additionally, the physical and chemical properties of the spent catalyst with deposited fines were studied. Brunauer Emmett Teller (BET) analysis showed that the deposition of fines on the catalyst did not affect the textural properties of the catalyst significantly. The Pore size and pore volume of the spent catalyst with and without fines did not differ; however, there was a slight reduction in the surface area and this was due to the agglomeration of fines at certain regions on the catalyst. Scanning electron microscope images of the spent catalyst showed larger agglomerates formed at higher temperature during hydrotreating as compared to small deposits at low temperature. Fourier transform infrared spectra of the spent catalyst suggested chemical interaction between the catalyst and the alumina silicates (kaolin). Thus, it could be inferred that the deposition of the fines on the catalyst is due to both physical adsorption of the fines as well as their chemical interaction with the hydrotreating catalyst. The regeneration experiment showed no improvement in the catalyst activity after the fines were removed from the catalyst surface which further supports that there was a chemical interaction between the catalyst and the fines. It was found that there is a chemical as well as physical interaction between the hydrotreating catalyst and the model fines.

Keywords: Hydrotreatment; process optimization; fine particles deposition; kaolin; catalyst fouling; pressure drop; statistical modeling.

Acknowledgements

I am extremely thankful to my supervisors Dr. A. K. Dalai and Dr. John Adjaye for their constant support and encouragement. The lucidity with which they impart knowledge and guidance is indeed a blessing. I am also indebted to my advisory committee members; Dr. Richard Evitts and Dr. Yongfeng Hu, for all their time and valuable suggestions that helped me trace the right path for the successful completion of this project. I feel extremely thankful to Dr. Lee Wilson for agreeing to be the external examiner for this work.

I owe a mention to Dr. Sandeep Badoga for helping me throughout the course of this work and Dr. Jackson Chitanda for teaching me certain laboratory skills. The ever-ready technical support of Mr. Rlee Prokopishyn, Mr. Richard Blondin and Ms. Heli Eunike is greatly appreciated, particularly, while dealing with reactor modifications and instruments; that too with a big smile regardless of the complexity of the problem.

Working in the catalysis and chemical engineering laboratory would never have been so stimulating without the support and dynamism of the colleagues. I feel gratified to have evolved working with each one of them.

I have always felt that my teachers, professor and mentors right from school to the university hold a very significant role in my overall growth as a student. I want to express my heartfelt gratitude to all those from whom I have attained knowledge and imbibed experience. Mrs. Veronica Carvel (school principal), Dr. K.S. Rana (paternal grandfather) and Mr. Digamber Singh (maternal grandfather), have always been a great source of inspiration and will always be.

I would also like to acknowledge the caring and affectionate friends I have who have always contributed in beautifying the journey of my life. It is the confidence of my parents in me that has always been my strength and I can never thank them enough. In the end, I can only thank God for blessing me with such wonderful parents and people in my life.

Dedicated

to

my parents and grandparents

for their undeterred support and motivation

throughout my academic endeavours

Table of Contents

List of Figures

List of Tables

1. Introduction

According to the reports by the international agency, the global demand for oil is expected to increase from 95 million barrels per day in 2016 to 105 million barrels per day by 2030 (www.eia.gov, 2016). The depleting conventional resources cannot independently meet this growing demand and this lays emphasis on the exploration of the unconventional crude oil resources (Giesy et al., 2010). Canada has the second largest oil reserve in the world; this primarily includes the oil sands in Athabasca basins that cover the area from the north-eastern Alberta and Saskatchewan (Dunbar 2009).

Bitumen is the highly viscous mixture of hydrocarbons, silica sand and clay minerals which is extracted from the oil sands. Further processing of bitumen, through primary and secondary upgrading, yields light gas oil (LGO) and heavy gas oil (HGO) product. The gas oils are further refined in the hydrotreating unit at high temperature (355-395 °C) and pressure (1000-1400 psig) to remove sulfur and nitrogen and to saturate the aromatics to produce synthetic crude oil (SCO). This helps in making the crude oil compatible with the stringent environmental regulations.

When bitumen-derived gas oils are hydrotreated, the entrained fines (clay particles that surface-adsorb organic coating) that are less than 20 μm pass through the guard-bed filters and enter the hydrotreating unit with the feed stream. Out of the several challenges faced during the synthesis of synthetic crude, the entrainment of these fines that deposit over the catalyst bed and cause a sudden pressure drop in the reactor is a significant one. When the reactor pressure drops due to catalyst fouling the ripened bed is replaced and this leads to operational problems and economical losses to the industry. Hence, it is significant to strategically study and analyse the possible measures to address this problem.

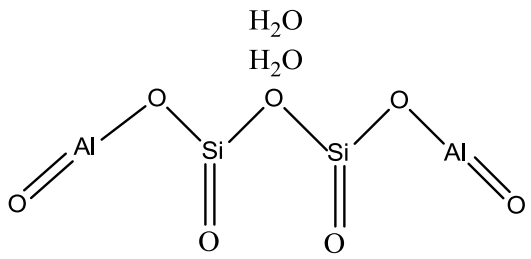


Figure 1.1 Kaolin Clay Structure

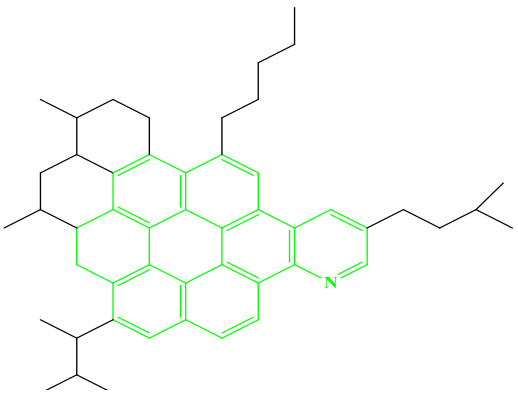


Figure 1.2 Asphaltene (Organic coating) Structure

1. 1 Background of the Project

The nature of fine particles impacts their interaction with the catalyst (Wang et al, 1999). Fine particles in the bitumen-derived gas oils are found to be similar to asphaltene coated kaolin. At the reaction conditions, the organic coating (asphaltene) of the clay particle (kaolin) desorbs and this causes the clay particles to drop on the catalyst bed leading to their eventual accumulation (Wang et al., 1999). Furthermore, the hydrotreating products such as ammonia, hydrogen sulfide and water were assumed to contribute in the deposition of fine particles on the catalyst bed. However, the water released during hydrodeoxygenation (HDO) displaces asphaltene molecule from the surface of asphaltene coated kaolin. This exposes the solid surface to more hydrophilic areas; thus increasing the tendency of fine particles to deposit on the catalyst bed (Wang et al., 2001).

Additionally, particle deposition is believed to be significantly impacted by the process conditions within the reactor. Process variables that can influence the particle deposition are temperature, pressure and reaction time. Also, the variation in particle loading of the feed and particle size can be of interest in determining the impact of particle deposition. There have been several studies that suggest that there is a pressure drop build-up in the reactor due to fines deposition (Iliuta et al.,2003). In fact the incidence of particles agglomeration was evaluated on the basis of increase in the pressure drop as a function of time (Iliuta et al., 2003). Several models have been derived for the pressure build-up and dynamics of the fine particles in the packed column (Gray et al., 2002; Iliuta et al., 2003). Particle deposition requires its arrival to the catalyst surface followed by catalyst-fines interaction that leads to the attachment of these fine particles to the catalyst (Gray et al., 1999). Perhaps the process conditions can be optimized to hinder the interaction between the catalyst and the fine particles.

Nowadays, the escalating energy demand and competitive oil market lay emphasis in supplying fuel at the most economical prices. Countries like Canada lack sweet crude unlike the middle-east; hence to stand as a potential oil supplier it has to develop resources and techniques to cut down the cost of exploration, production and processing. Therefore, any advancement and contribution in this can help in reducing the economical strains on the oil industry in processing bitumen-derived oil and is of great impetus to Canada. Classical approach to this was to invent catalyst with high activity and selectivity (Badoga et al. 2014; Ferdous et al. 2007; Ferdous et al., 2004). The best hydrotreating conditions for various oil streams have also been established (Botchwey et al., 2004). However, issues related to

catalyst fouling still hold a significant room for improvement. Thus, in this work, the impact of hydrotreating process conditions, such as temperature (355, 365 and 375 °C) and pressure (1200, 1300, 1400 psig), on the fine particle deposition within the catalyst bed has been studied. Conventional statistical tool, Centre Composite Design, is used to design the experiments and develop models for bed deposition and sulfur conversion.

1.2 Knowledge Gaps

Based on the literature review discussed in chapter 2, much research has been done on pressure drop studies in the hydrotreating reactor (Gray et al., 2002). However, majority of this has been focused in developing models for pressure drop and relating it with the advent of particle deposition. The individual and combined effects of process parameters on particle deposition have not been widely studied. Detailed research is necessary to investigate the optimum operating conditions for hydrotreaters to reduce pressure drop problems due to particle deposition. Most research does not lay emphasis on finding the best process parameters while keeping the sulfur conversion of the feed uncompensated.

Details of the physical and chemical interactions between the fine particles and the catalyst are limited in the literature. However, it is essential to know what causes the fines to settle on the catalyst. Also, the impact of varying particle loading in the feed and the particle size on their deposition on the catalyst bed has not been studied at hydrotreating conditions. The impact of fines deposition on catalytic activity has not been reported clearly in the available literature.

1.3 Hypotheses

Process parameters, specifically the temperature will have a dominant impact on particle deposition. The operating conditions for hydrotreating can be optimized to give minimum bed deposition without altering the catalyst activity.

The catalyst has a physical as well as chemical interaction with the fines and the variation in particle loading, chemical nature of the particles and particle size will impact their deposition on the catalyst.

1.4 Objectives

This research aims at finding the impact of hydrotreating process parameters on fine particle deposition that are present in bitumen-derived light gas oil (LGO) on the catalyst. This objective was divided in two sub-objectives (Phase 1 and 2)-

Phase 1: To study and optimize the impact of process parameters (temperature, pressure and particle loading) on kaolin deposition with varying particle loading in the LGO feed.

Phase 2: To study the deposition trend of asphaltene coated kaolin in the catalyst basket (catalyst bed) and the impact of particle deposition on the chemical and physical properties of the catalyst.

1.5 Thesis Organization

Chapter wise presentation of the thesis is as follows: Chapter 2 discusses the detailed literature related to this research to provide the relevant information, and lead to knowledge gaps, hypotheses and objectives of this research. Chapter 3 presents the experimental details including materials and methods used such as catalyst preparation, hydrotreating runs and characterization techniques. Chapter 4 explains in detail the results and discussions from the first sub-objective; where different loadings of kaolin were used as model fines to study the impact of process parameters. Chapter 5 includes the results and discussion from the second sub-objective; where asphaltene coated kaolin was suspended in the feed to study the deposition trend and interactions. Chapter 6 lists the research conclusions along with recommendations for future work.

2. Literature Review

This chapter includes a review on the significant concepts of hydrotreating and focuses on the emerging challenges in hydrotreating bitumen-derived gas oil. Having discussed the basic concept of bitumen upgrading and hydrotreating in the introduction, the relevant research in scope for this study has been reviewed. Also, the specific challenges that arise while dealing with bitumen-derived gas oils due to fine particle accumulation have been cited. The factors that may cause catalyst fouling, specifically fine particles have been discussed.

2.1 Athabasca Bitumen Upgrading and its Chemical and Physical Properties

Post oil sands mining, the bitumen extraction and upgrading are the major step in oil refining. Bitumen is a viscous, black, sticky mixture of organic liquids (hydrocarbons) that are composed primarily of highly condensed chemical compounds (www.saocl.com 2010). It is extracted as a by-product or residue of the fractional distillation of crude oil. It is a form of petroleum with highest boiling point and viscosity (Zhao et al., 2002). The definitions of heavy gas oil fractions and bitumen on the basis of physical properties is given in Table 2.1.

Table 2.1 Physical properties of heavy oils and bitumen (Gray et al., 1994)

Fraction	Viscosity (mPa.s)	Density (g/cm^3)	API gravity (^{o})	Boiling point (°C)
Heavy Oil	10^2-10^5	0.935-1.0	10-20	350-650
Bitumen	$>10^5$	>1.0	<10	525-675

Liu et. al., studied the processability of oil sand ores in Alberta, they stated that the physical and chemical properties of the ore dictate the extent of bitumen liberation; also the extent of fine particles holds an important role. Poor processing ores showed surface properties such as zeta potential; along with higher induction time for bitumen and air bubble, and colloidal properties between bitumen and silica. The slime coating (adsorption of fines to bitumen) was observed to be the main reason for poor processability of the high fine ores (Liu et al., 2005).

Zhao et al., compared the Athabasca bitumen with conventional and heavy crudes. In their experiment they prepared the narrow cut fractions of bitumen pitch by the technique of Supercritical Fluid Extraction (SCFE) with pentane. The temperature was less as compared to the thermal process. Along with Athabasca bitumen, Venezuelan heavy oil, Saudi Arabian

light crude oil and Chinese Daquing conventional crude were used. It was reported using various characterization techniques such as XPS and GPC, the end-cuts from Athabasca bitumen contained more solids (7 w/w%) than the other crudes. Nano-sized alumino silicate clay particles were present; these were non-uniformly covered with a polar and aromatic organic matter that was insoluble in toluene (Zhao et al., 2002).

Selucky et al., reported the results of a detailed study of maltenes, the deasphalted bitumen from McMurray. Bitumen was extracted from the sand using soxhlet with benzene as the solvent. The asphaltene was precipitated using pentane in a centrifuge at 2800 rpm under N_2 for 12 hrs. The deasphalted bitumen was set for column chromatography on silica and then alumina and silver nitrate was used for the column chromatography of pentane eluate from silica. The straight chains of paraffins were separated on molecular sieves non-adduct. The extracted oil sands yielded 16.6% asphaltenes and the deasphalted oil content was 83.4% (Selucky et al.,1977).

A series of papers on the chemical composition of Athabasca bitumen were published. The study was conducted to understand the chemical composition of distillable aromatic fraction. An extensive fractionation of the bitumen was carried out; this involved precipitation, extraction, adsorption, complexation and adduction chromatography along with molecular distillation to separate asphaltene from maltene. Using chromatic method it is possible to isolate an aromatic and further separate it to mono, di, tri and poly aromatic sub-fractions. The sample was found to contain 38.6% aromatics; 76.4% of the aromatic fraction was distillable at 10^{-3} Torr and 240^{o}C (Strausz et al., 2011).

A sample from Fort McMurray Alberta Canada (located 18 m below the surface) was collected (Strausz et al., 2010). This sample was from the Syncrude High Grade (SHG) oil sand containing 12% bitumen. The bitumen was extracted by using soxhlet with CH_2Cl_2 as the solvent. They studied the chemical composition of the saturate fraction taken from Athabasca bitumen. The yield of asphaltene was 17% of the total bitumen content. Fluorescence imaging micro-spectrophotometer (FIMS) Spectrum along with the gravimetric composition and carbon number maxima was used to determine the concentration distribution of the alkanes (mono-hexacyclic) on the basis of carbon number. The biodegradation severity was found to be in the following descending order Grosmont, Athabasca, Peace River and Lloyddminster. The distillables and non-distillables differ in molecular size, chemical composition or possibly both. NMR of distillable sub-fraction indicated a low ratio of mid-

chain methylene over the chain end methyl resonance. This manifested the absence of long alkyl chains in distillable saturated sub-fractions. It was suggested that more than distillable fraction, it was in the non-distillable fraction that contained the aromatic carbon; however in trace amount only.

A study on the physical properties and extraction measurements for Athabasca bitumen and light hydrocarbon system was conducted (Nourozieh et al., 2011). Liquid upgrading process was used for upgrading bitumen, ethane was the solvent. The process proceeded in 2 phases- solvent enriched and the other bitumen enriched. The parameters affecting the extraction yield were pressure, temperature and solvent to bitumen ratio. The reaction was carried out at 21.6 °C with 725 to 1305 psig at 4 different ethane concentrations. The study supported that the extraction yield increased with increased pressure. Solvent to bitumen ratio variations showed that with an increased concentration of ethane more light components were extracted. Same experiment when carried with propane as the solvent gave better yield than ethane at similar conditions. This was owing to the nature of propane that enabled it to extract more components to solvent enriched phase as compared to ethane.

The recent advances on process technologies for upgrading of heavy oils and residua were compiled (Rana et al., 2007). The 2 types of residue are Atmospheric Residue (AR> 343 ^{o}C) and the Vacuum Residue (VR>565 ^{o}C). It is reported that at a lower temperature with constant solvent composition and pressure the yield increases but the quality degrades. Various techniques used in upgrading are discussed; Gasification is the complete cracking of residue into gaseous products. Delayed Coking is the complete rejection of metals and carbon while enabling partial conversion to liquid product (naphtha and diesel). Fluid Coking is slightly better than delayed coking due to the advantage of a slightly improved liquid yield and economic benefits. In Flexicoking, excess coke is converted to syngas at about 1000 $^{\circ}$C, this temperature is sufficient enough to burn all the coke. It is an extended form of fluid coking.

Visbreaking is a rather mature process that can be applied to AR, VR and solvent deasphalter pitch and this gives a mild improvement in the viscosity. It is popularly used to improve the refinery net distillate yield. The thermal process is used to produce large amount of low value by-products and also requires extensive processing of its liquid yields. For this reason the catalytic residue process are more popular. The Fluid Catalytic Cracking (FCC) converts a significant portion of the heavier fractions of oil to high octane gasoline components. In

hydroprocessing of the residue a substantial amount of hydrogen is consumed. It has a high product selectivity and better product yield (85% higher) (Rana et al., 2007).

For the final upgrading of bitumen to make it commercially ready product, it should be processed to lighter hydrocarbons. The yield is generally termed as synthetic crude oil. The upgrading process is divided into 2 major steps namely, primary and secondary upgrading process. After primary and secondary upgrading the light gas oil and the heavy gas oil streams are sent to the hydrotreating units for further processing.

2.2 Hydrotreating Process

Hydrotreating is a catalytic hydrogenation process used in refining or purification of fuel and other by-products. The emphasis is on improving the quality of the final product. Hydrotreating uses hydrogen at high pressure and temperature in the presence of a metal catalyst for the removal of unwanted constituents of the crude oil. A representation of the hydrotreating reaction could be:

$$\textbf{Feed} \xrightarrow{H_2,\ T,\ P,\ Catalyst} \textbf{H/C} + \textbf{H}_2\textbf{S} + \textbf{NH}_3 + \textbf{H}_2\textbf{O} \qquad \textbf{(2.1)}$$

The major objectionable components that are desired to be removed during hydrotreating are sulfur, nitrogen, olefins and aromatics. The addition of hydrogen helps burn the olefins as clean-burning paraffins. Naphtha and other light materials are treated in the catalytic reforming units; whereas, the heavy material is further treated to meet the quality standards for use as commercial fuel oil. This heavy stream has a high content of unwanted sulfur, nitrogen, metals, unsaturates and other hetro-compounds; hydrotreating plays a significant role in upgrading it to environmental and commercial industry standards (Satterfield 1996).

The removal at every step of hydrotreating is giving a specific term; the removal of sulfur in the form of H_2S is termed as hydrodesulfurization (HDS). The organo-sulfur compounds react with hydrogen and the polluting sulfur gas is liberated in the form of H_2S thus making the product compatible with the environmental standards. However, removal of nitrogen is for entirely different reasons. It is seen that organo-nitrogen compounds tend to deactivate the hydrotreating catalyst hence hydrodenitrogenation (HDN) is used to remove such unwanted

hetro-compounds of nitrogen in the form of NH_3. The other reactions that take place in a hydrotreating reactor are hydrodemetallization (HDM), removal of metals such as arsenic, nickel and vanadium, and hydrodeoxygenation (HDO), removal of oxygen in the form of H_2O. The pre-treatment of petroleum fractions for the downstream processes is essential for avoiding catalyst poisoning by hetero-atom contamination (Leffler 2000).

Hydrotreating is basically carried out in the presence of a commercial catalyst. This catalyst plays a vital role in determining the conversion, product quality and the economics of the reactor. Thus, a brief study introducing the hydotreating catalyst and the concept of catalyst fouling has been covered in the next section.

2.3 Hydrotreating Catalyst and Catalyst Fouling

Catalyst is primarily used to accelerate the speed of a chemical reaction. Catalysts have active sites for a particular reaction which adsorb the reacting species and desorption occurs for the product moieties. This can be explained as a cyclic process (Santen et at., 2006) in which the participating catalyst remains unchanged at the end of the reaction. A catalyst functions by decreasing the activation energy for a reaction without altering the equilibrium (Coulier et al., 2001).

The significance of using a catalyst during the hydrotreating process lies in its applicability in removing the unwanted constituents in the feed such as sulfur, nitrogen, etc to an appreciable level and also to increase the rate of hydrotreating reaction to a better conversion to lighter products. The typical desirable properties of these catalysts are high surface area, larger number of active sites, thermal and chemical stability, selectivity, suitable shape and pore-size. These catalysts are active components of Mo or W, generally in combination with a suitable metal promoter (eg. Ni, Co, Fe) and an alumina or silica support. Support is used to give mechanical strength to the catalyst (Satterfield 1996).

The type of catalyst used during a hydrotreating reaction depends on the product desired. $NiMo/\gamma Al_2O_3$ and $CoMo/\gamma Al_2O_3$ are two of the most widely used commercial catalysts for hydrotreating. NiMo sulfide catalysts are more suitable for HDN and CoMo sulfides for HDS (Topsoe et.al., 1996). For most of the HDT reactions the commonly used active phase is MoS_2. Much has been experimented on the potential catalyst for hydrotreating reaction. Zeolites have also found great deal of application in this field. There is a wide variation in the size, shape, pores and material of the catalyst synthesized for the enhancement of the product

yield and quality. For the heavy oil feeds, the use of highly active catalysts was reported ie., New Bulk Activity (NEBULA), Exxom Mobil and Super Type II Active Reaction Site (STARS), Akzo Noble Catalyst (Rana et al., 2007). This forms a relevant and wide field of research with numerous research papers being published.

Over the period of reactor runs during hydrotreating reaction the catalyst tends to foul. The products or by products could be a reason for this or even the contents of the feed depending on the feed taken and on the hydrotreating conditions. In fact, catalyst deactivation due to fouling is the main focus while designing and preparing catalysts for hydroprocessing of different feeds. HDT catalysts are more prone to the pore mouth plugging and hence they are often seen to be used with guard-bed catalysts with large pore diameter, high metal retention and low surface area (Rana et al.,2007). Even though several measures are taken catalyst plugging cannot be avoided during hydrotreating but it is desirable to avoid a quick catalyst plugging during reactions and also the catalyst is preferred to be regenerated so as to enhance the productivity of the process and reduce the expense of catalyst replacements. The major constituent for catalyst fouling is the coke that is formed during the reaction, nitrogen organics, metals and ultra-fines in the feed (Esmond, 1974).

Just like any other crude oil processing hydrotreating is extremely essential for the Athabasca bitumen as it contains high sulfur and nitrogen organics content (Zhao et al.,2002). However, for the hydrotreating of the Athabasca bitumen the major challenge is the catalyst fouling due to the fine particles deposition. The amino-silicates present in the form of asphaltenes and the humic clay that is similar to kaolin are the major contents of these fines (Wang et al.,2001). In the forthcoming section these fines and their characteristic have been reviewed; along with their effect on the hydrotreating catalyst.

2.4 Organic Coated Solids in the Bitumen Feed

This section deals with the organic coated fines that exist in the bitumen feed and their inhibiting effect on bitumen hydrotreating. It is a matter of foremost concern in the upgrading of Athabasca bitumen to avoid catalyst plugging due to the deposition of these fine particles on the catalyst surface and in the pores. Sparks et al. categorized the bitumen solids as: ultra-fine clays, fossils, heavy minerals and aggregate. (Sparks et al.,2003).

During the hot water extraction process (HWEP) of bitumen extraction from oil sands; bitumen gets attached to air bubbles thus the formation of bitumen rich froth takes place. The

bitumen extraction can be as high as 93% for good ores. However, for poor processing ores, the high content of fines (40 wt% fines in total solid content) and divalent ions causes a technical challenge for the effective bitumen extraction (Liu et al., 2003)

Table 2.2 Composition wt% of oil sands samples (Liu et al., 2005)

Oil Sands	Bitumen	Solids	Fines in solids (<44µm)	Water	Source
Good processing ore	12.6	80.7	9.6	6.7	Syncrude
High electrolyte ore	12.8	86.4	10.2	0.8	Syncrude
High fines ore	6.3	86.6	40.4	7.1	Syncrude
Weathered ore	15.3	83.2	4.8	1.5	Suncor

Focusing on the impact of fine particles on hydrotreating catalyst, the fines and the asphaltenes present in the Athabasca bitumen feed are discussed in the forth-coming section.

2.5 Fines

The origin of fines could be the iron sulfides from upstream equipments, naturally occurring fine clays in oil sands bitumen and in situ coke fines or organic precipitates. There is a huge scope for the study of these fines accumulation and for planning and proposing strategies against reactor plugging (Iliuta et al., 2003). The clay crystallites with a size of less than 300 nm and of thickness of less than 10 nm are reported to be particularly problematic material (Kotlyar et al.,1999a). These are the major contributor to non-filterable ultra-fines found in the bottom tailings and in bitumen feed stream (Sparks et al., 2003).

In an undisturbed state these fines generally cover the industrial solid surface; whereas when the fluid saturating the catalyst pore is set in motion these fines are entrained and later deposited at a convenient accumulation site leading to plugging (Gruesbeck 1982). The major content of these fines are the clay particles that are called the humic clays and these are found to be similar to asphaltene coated kaolin particles (Wang et al.,2001). The bitumen feed entering the hydrotreating reactor is pre-treated using techniques such as desalting, distillation

and also filtered to remove most of the unwanted particles; however, the ultra-fines (particles <20μm in diameter) can persist in the feed stream owing to their non-filterable size (Wang et al., 1999).

Kaolinite is the most abundant clay in oil sands. It is a layered alumina silicate with tetrahedral sheet that has oxygen linking atoms binding it to the octahedral sheet of alumina in the ore. It was found that the adsorption of asphaltenes had a relevant impact on the fines interactions. Also, the major interacting forces were van der Waals forces, double layer repulsive forces and electrostatic forces (Wang et al.,1999), (Murgich 2002), (Mendoza et al.,2009). The deposition of particles to a substrate is governed by the size of the particles. Fine particles can plug the pores of the catalyst whereas the larger ones settle on the surface and this is governed by the physical forces arising from gravity and fluid drag (Elimelech, 1990).

Some of the important factors that govern the fines deposition are: particle size, fluid velocity, physical properties of the fluid and porous solid (Gruesbeck, 1982).
It is essential to study where exactly on the catalyst do these fines entrain and deposit during a hydrotreating reaction. The local laws of entrainment of the fine particles were studied and reported; the particle size determining the fraction of fluid pathway which was found to be plug type (Gruesbeck, 1982). It is suggested that the clay particles in bitumen feed have a tendency to adsorb asphaltenes and agglomerate. The adsorption of asphaltene layer over the clay particles is non-uniform and patchy (Sparks et al., 2003).

Ultra fines are generally coated with asphaltenes and this gives a reason to study the role of asphaltenes in hydrotreating the bitumen feed and also understand the surface chemistry that comes into play when asphaltene coats the humic particles and get adsorbed on the catalyst surface.

2.6 Asphaltenes

Asphaltenes are the target molecules responsible for deactivating the hydrotreating catalyst in either fixed or moving bed operation. The exact chemical structure of asphaltene is not known however, several structures have been proposed. It exists as one of the common uncertain molecule in heavy oil and bitumen. Asphaltenes can be considered as large aromatic sheets having high molecular weight which are layered up on one another to form a unit cell and larger asphaltene molecules. These asphaltenes cover the fine particles associated with

bitumen feed (Rana et al., 2007). Asphaltenes from same source is expected to have same molecular dimension; though the chemical structure may differ if the sources and unit sheets differ (Gawel et al., 2005).

Asphaltenes are formed by aromatic compounds having a π- π interaction that undergo an acid-base interaction and are self-associated by hydrogen bonds (Chang and Fogler 1994). Asphaltenes are tightly bound to bitumen solids evident by high Ni and V concentration detected as compared to ultra-fines from fine tailings. In asphaltenes they occur as chelates or porphyrins of Ni and V. Fe and S can also be present (Kotlyar et al., 1999).

The concept of aggregates and micelle formation in case of asphaltenes was studied. A micelle is a reversible aggregate formed in a polar environment that remains constant in size for a set of given environmental constraints. The term critical micelle concentration (CMC) explains the concentration at which asphaltene molecules begin to self-aggregate in a certain polar media. In a paraffinic environment (non-polar media) larger, non-dissolvable asphaltene agglomerates are formed (Haraguchi et.al., 2001).

Asphaltene adsorption on solid substrate is essential to study due to the effects on wettability of the minerals affecting fluid permeability in rock reservoirs. The interaction of asphaltene and kaolin is studied and the surface chemistry was reported (Wang et.al., 1999); the asphaltene coated kaolin gives deep-bed filtration due to steric repulsion and without asphaltene coating the kaolin clay particles gave cake filtration. It is difficult to comment if an interaction would take place between asphaltene molecules or the aggregates formed (Haraguchi et.al., 2001).

An artificial model of fine particles to study the effect and filtration trend of fines on catalyst surface and within the pores was developed. The fine particles introduced in the bitumen feed were asphaltene coated kaolin. The surface chemistry was studied and an illustration of the deposition mechanism is shown in Figure 2.1. It was suggested that the adsorbed organics on the clay were desorbed in water and led to the flocculation of the clay particles on the collector (catalyst) surface (Wang et.al., 1999 and 2001). Asphaltene coated kaolin is commonly used in fine particles studies. The trickle bed reactor is widely used for the commercial purposes; owing to the wide range of the operating condition it caters to. However, it shows complex behaviour due to hydrodynamic characteristics that arise from the gaseous and liquid flow in the packed bed (Wang, 2000).

The effect of hydrotreating product in deposition of fine particles on the packed column of the reactor was reported. Fine particles that cause reactor plugging in the reactor bed at hydrotreating conditions of temperature and pressure were studied. Ammonia and quinoline were found to have no effect on the particle deposition in the reactor. From this it could be concluded that HDN did not affect the particle behaviour; whereas, HDS, HDO, HDM had an effect on the particle deposition owing to the hydrogen sulfide, water and metal oxides formed (Wang, 2000).

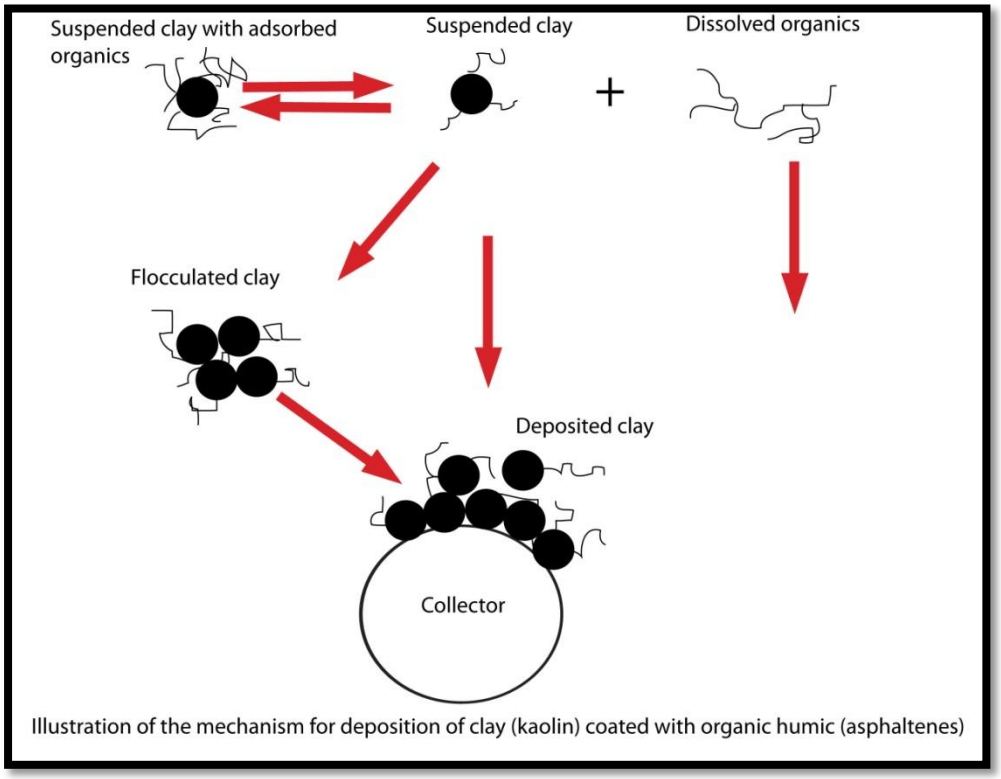


Figure 2.1 Asphaltene kaolin surface interaction model

Thus, it is shown that fine particles and asphaltenes play a significant role in hydrotreating reaction due to their nature of plugging the catalyst. However, the reactor used in hydrotreating and the operational problems associated with catalyst fouling due to fine particles deposition are essential to understand so as to provide a better incentive to the Athabasca bitumen upgrading. The next section deals with the problems associated with fine particles deposition and the effect on reactor conditions.

2.7 Theory of Particle Deposition

The deposition of particles to a substrate is governed by the size of the particles. Fine particles can plug the pores of the catalyst; whereas, the larger ones settle on the surface and this is governed by the physical forces arising from gravity and fluid drag (Elimelech and O' Melia, 1990). The forces of attraction that majorly govern the fine particles and catalyst interaction are van der Waals forces and double layer repulsion (Chowdiah et al., 1981; Elimelech et al., 1990).

The effect of flocculation time on the structure and size of model clay fines (kaolinite mix) was studied. The study led to the understanding that the flocculation kinetics depends on aggregate size density, these aggregates grow rapidly to form enormous open structure in the early stages and the aggregate density tends to increase slightly at prolonged flocculation times (Vaezi et al., 2011).

The particle capture in a packed-bed reactor was studied; depending on the size of the particles and catalyst pore diameter, deep-bed and granular filtration was observed (Narayan et.al., 1997). The pressure drop increased with fines deposition in all cases; however the intensities varied. The efficiency of trapping the fines was reported to change with deposition ie., an increase in deposition as bed 'ripens'(Deb, 1996; Wnek et.al., 1975). The three main phases of the particle deposition are: the smooth covers that include the trapped particles on the surface of the collector, multi-layer deposit and finally, the particles may clog the catalyst pores in the bed and straining (cake filtration) acts as a dominant mechanism (Choo et.al., 1995). When gas and liquid phase flow concurrently downwards through packed bed of solid particles it is a complex situation. The prevailing flow regime is the function of the followings: (1) Gas and liquid flow rate; (2) Reactor dimensions; (3) Particle size and shape; (4) Packing and (5) Thermo-physical properties of gas and liquid (Choo et.al., 1995).

Asphaltene coated kaolin was mixed in the bitumen extracted gas oil feed to substitute the fine particles and the deposition trend was reported. Asphaltene coated kaolin gives deep-bed filtration whereas non-coated kaolin gives cake filtration. The steric resistance against multilayer deposition acting in case of the asphaltene coated kaolin led to a greater resistance to deposition than in case of non-coated kaolin (Wang et al., 1999, 2001).

In the specific case of asphaltene coated kaolin, the study showed that the deposition increases with the progress of the catalytic reaction; in the high-temperature zones the efficiency of filtration will be higher as compared to the lower reactor zones. This explains the greatest

deposition of fine particles at the exit of the reactor. As the reaction proceeds, the ratio of the liquid to gas reduces which further enhances the particle deposition (Wang et.al., 1999). Variables such as reaction kinetics, heat and mass balance, bed porosity, catalyst shape and size, wettability, interfacial tension, gas and liquid flow rates, viscosities have a considerable effect on the operation of the reactor (Wu et al., 1996).

2.8 Impact of Hydrotreating Reaction Conditions on Particle Deposition

Working on trickle bed is highly common for hydrotreating of bitumen-derived products. The hydrotreating reaction conditions require high pressure (6-12 MPa H_2) and temperature (355-395^oC) and the catalyst that is commonly used is $NiMo/\gamma Al_2O_3$. There have been relevant studies explaining various steps of the hydrotreating process; however, not much has been studied about the trend of the fine particle deposition despite the operational problems related to this. Little work has been done to understand the filtration of these fine particles, how they affect the pressure drop (Gray et al.,2002).

Even small quantities of fine particles could increase pressure drop in the packed column (Chan et al.,1994). It was reported by Iliuta, 2003 that the incidence of fines deposition could be appropriately evaluated by the pressure drop rise as a function of time and also in terms of the plugging for local porosity and in terms of specific velocity versus bed depth. The impact of fine particles, in terms of pressure drop, as a function of time, was analyzed and also the plugging pattern and the concluding remarks were as follows (Ranade et al.,2011):

- Two-phase (liquid feed and H_2) pressure drop and the volume-average specific deposits shoot up with an increase in the liquid flow rate.
- Density of gas used in the reactor is not a determining factor for particles deposition.
- Two-phase pressure drop ratio increases with a decrease in liquid velocity.
- Two-phase pressure drop ratio goes down with a decrease in the concentration of the inlet fines.
- Two-phase pressure drop ratio increases with an increase in the fines diameter.

In a trickle-bed reactor, 2-phase (liquid feed and H_2) pressure drop along the length of the bed is a function of (Ranade et al.,2011):

1. Reactor hardware e.g. column diameter, particle size and shape and internal assembly.
2. Operating parameters e.g. gas-liquid flow rates.

3. Fluid properties like density and viscosity of the flowing fluid, surface tension and surface characteristics.
4. Operating temperature and pressure indirectly affect the pressure drop.

Hydrotreating conditions (catalyst, temperature and hydrogen) will have a significant effect on fine particles deposition (Wang 2000). The particle-particle interaction between the fines and its impact was reported (Wang et al., 2001). The surface chemistry of the fine particles was also reported. The experiment was conducted in a batch reactor. Along with the filtration trends, Wang, also reported the mechanism of kaolin and asphaltene behaviour in a suspension as shown in Figure 2.1. The impact of process conditions can be an essential parameter for the fines deposition. However, the catalyst-fines interaction and the impact of temperature and hydrogen partial pressure have been poorly reported in the literature.

A detailed study on the impact of pressure and temperature related to particle deposition is not available in the literature. Apart from the pressure drop due to fines plugging not much has been investigated on the temperature or the range of temperature at which the maximum fines deposit or the hydrogen partial pressure that results in maximum fines deposition.

3. Experimental

3.1 Materials

Tri-lobed gamma alumina support was supplied by Sasol, Hamburg, Germany. Nickel nitrate, molybdenum oxide, amorphous kaolin, butanethiol, toluene, heptane and hexane were purchased from Sigma Aldrich, Edmonton, Canada. 3 mm glass beads were supplied by Fisher Scientific, Edmonton, Canada. The Light Gas Oil (LGO) feed and bitumen was provided by Syncrude Research Centre, Edmonton, Canada. 0.22μm membrane filters were purchased from Millipore, Toronto, Canada.

3.2 Catalyst Preparation

The NiMo/γAl_2O_3 catalyst was prepared using sequential incipient wet impregnation method. Tri-lobed gamma alumina pellets were impregnated with 13 wt% of molybdenum using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as the precursor. The impregnated support was dried at 100 °C for 6 h and then calcined at 550 °C for 5 h. Then, 2.5 wt% of nickel was impregnated on the support using nickel nitrate hexahydrate as the precursor. After nickel impregnation, the support was dried at 100 °C for 6 h and then calcined at 550 °C for 5 h to obtain 2.5 wt% Ni 13 wt% Mo /γAl_2O_3 catalyst.

3.3 Experimental Setup

All the experiments were run in a batch reactor. However, a catalyst basket was used in static mode to pack the catalyst similar to the fixed bed reactor. To study the impact of fines deposition it is important to have a system that accelerates the deposition process so that the effect of process parameters can be studied and this can be most appropriately done using a closed system. In case of the industrial fixed bed reactor most of the fines, suspended in the feed, drain out with the product and hardly 2-3% of the fines are trapped in the catalyst bed (Chan et al.,1994). Thus, the study for fines deposition would take long time in a fixed bed as compared to a batch system. Therefore, in scope of time, this study was conducted in a batch reactor. Two 450 ml vessels were used: One for sulfidation and the other to switch the vessel containing sulfiding solution quickly with the vessel containing the LGO feed. The system was connected with a hydrogen inlet and the venting system, connected to aqueous NaOH scrubber (See Figure 1). A catalyst basket was used in its static mode to create a catalyst bed

in the batch system. This was done to have similar catalyst packing as in the trickle bed reactors for the deposition of fine particles. The basket was packed using glass beads, silicon carbide and tri-lobed NiMo/γAl_2O_3 catalyst as shown in Figure 3.1. The impeller blades were modified and so was the impeller shaft to get a vertical flow of the liquid in the reactor so that the fines entrained feed could trickle down the catalyst packed in the basket (See Figure 3.2). Samples of the hydrotreated LGO were collected from the sample outlet. Thermocouple connected to the temperature sensor helped in maintaining the temperature inside the reactor vessel. Constant pressure inside the reactor was maintained with the help of a pressure regulator installed at the hydrogen inlet.

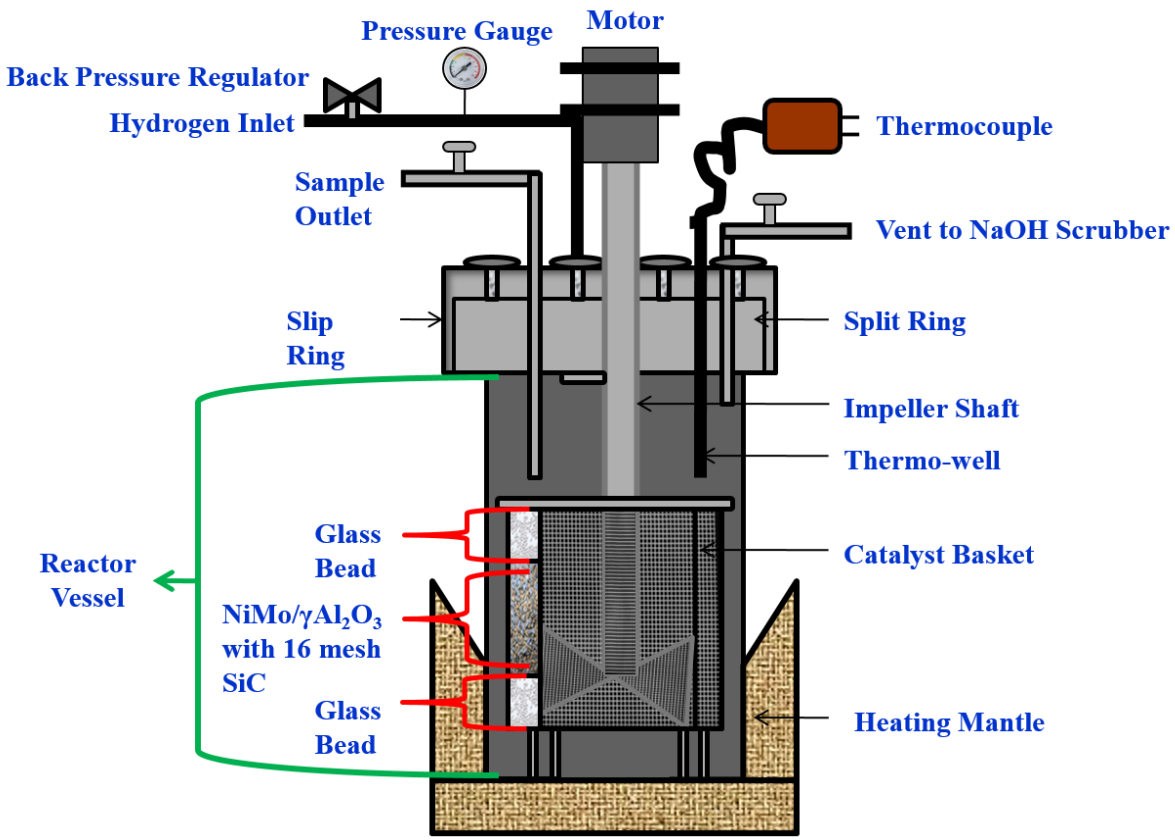


Figure 3.1 Schematic representation of batch reactor with catalyst basket in static mode

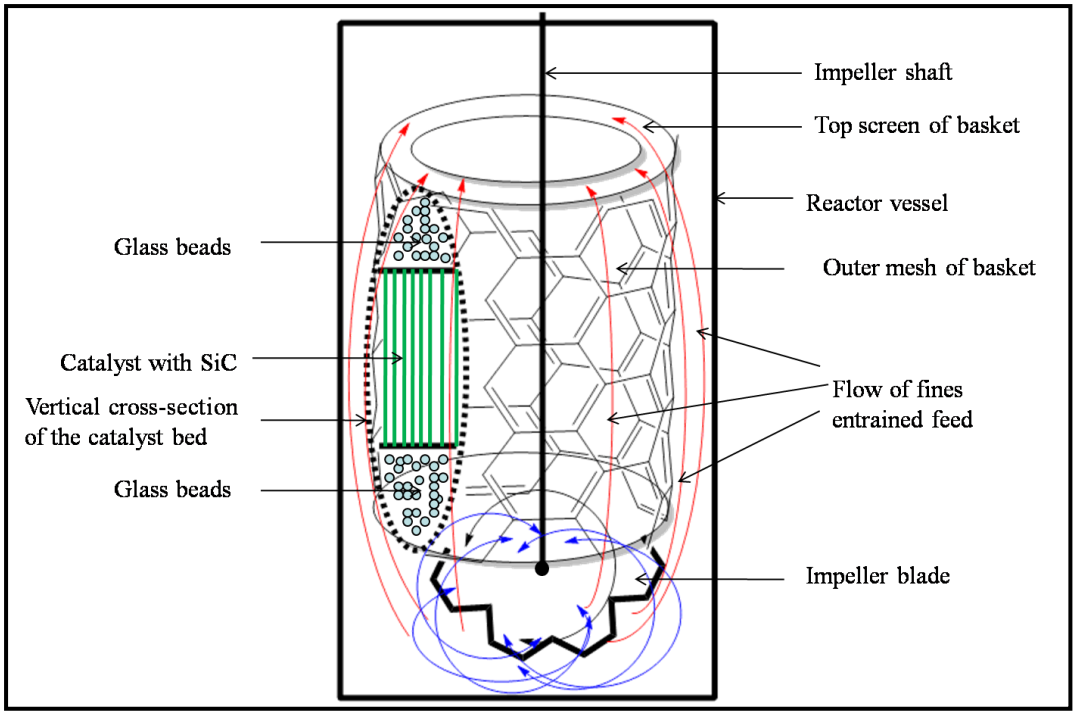


Figure 3.2 Flow of fines entrained feed through the catalyst basket in the reactor vessel

3.4 Sulfidation

The catalyst was packed in the basket, with 3 mm glass beads at the top and the bottom of the catalyst bed, and the catalyst mixed with silicon carbide is in the middle (See Figure 1). The catalyst basket was used in static mode and the impeller of the basket was used for constant stirring of the feed. 200 ml of cleaning oil was mixed with 8 ml of sufiding solution (butanethiol) in the 450 ml vessel which was attached with the reactor to start sulfidation of the catalyst. The catalyst was sulfided for 4 hrs. The reactor temperature was first ramped at 193 °C, the reactor was pressurized to 1000 psig with hydrogen and then stabilized at these conditions for 1.5 hrs. Then, the temperature was further increased to 343 °C and this temperature was maintained for 2.5 h and hydrogen pressure was stabilized at 1300 psig for this step. After 4 hrs of sulfidation the reactor vessel was left for cooling, and on reaching the ambient temperature, the reactor was depressurized (See Figure 1). The vessel containing sulfidation solution was replaced with another vessel with LGO feed, to hydrotreat the LGO with the sulfided catalyst.

3.5 Model Fines Synthesis

For the first sub-objective (Phase 1) commercial kaolin (alumino silicate) was used as model fines. The size range and the carbon content of kaolin particles are mentioned in Appendix A of this thesis. For the second phase, model fines were synthesized in the laboratory. Asphaltene was extracted from Athabasca bitumen and the procedure for the extraction of Asphaltene is explained in section 3.6 of this chapter. Commercial kaolin of two different sizes was coated with asphaltene to prepare two batches of asphaltene coated kaolin of varying sizes. The procedure for the same is explained in the next section of this chapter. The properties of asphaltene, kaolin and model fines used are reported in Appendix A.

3.6 Synthesis of Asphaltene Coated Kaolin Model Fines

The synthesis of asphaltene coated kaolin was divided into two major steps-

- Extraction of asphaltene from bitumen-

  To extract asphaltene form bitumen, soxhlet extraction process was used. The first step was to dissolve asphaltenes in toluene. Toluene was added to bitumen in a beaker maintaining 40:1 ratio. The mixture was stirred at room temperature till the highly viscous bitumen was completely mixed with the solvent (toluene). The mixture was then centrifuged at 3000 rpm for 1 h. Solvent in the supernatant was collected by drying the supernatant in a rotary evaporator. Thick viscous mass collected in the flask was dried at 70 °C overnight to remove volatiles. Remaining mass was then transferred to a thimble and the collected mass was washed with n-heptane to dissolve any remaining maltenes in the collected mass. Asphaltene is heptanes-insoluble and hence the mass left in the thimble after heptanes washing was asphaltene. The collected asphaltenes were vacuum dried at 70 °C overnight.

- Preparing Asphaltene coated kaolin (model fines)-

  For the synthesis of fines, 1:5 ratio of asphaltene to kaolin was used. To coat 30 g of kaolin, 6 g of asphaltene was dissolved in 1.5 L of toluene and the mixture was sonicated for 30 minutes. 1.5 L of heptane was added to the sonicated mixture of toluene and asphaltene and this was again sonicated for 20 minutes. Finally, 30 g of kaolin was added to the beaker and the contents of the beaker were maintained at an

agitation speed of 200 rpm for 24 h. Kaolin of two different sizes was coated with asphaltene in the same way in two different batches. After letting asphaltenes adsorb on kaolin overnight, the fines and the solvent mix in the beaker were filtered. The fines were collected on 0.22μm membrane filters. The liquid was passed through the filter twice to ensure all the fines were collected on the filter. Following this the fines were dried at 70 °C for 12 h. The prepared fines were characterized and stored in a desiccator (Wang 2000). A schematic representation of fines synthesis is shown in Figure 3.3.

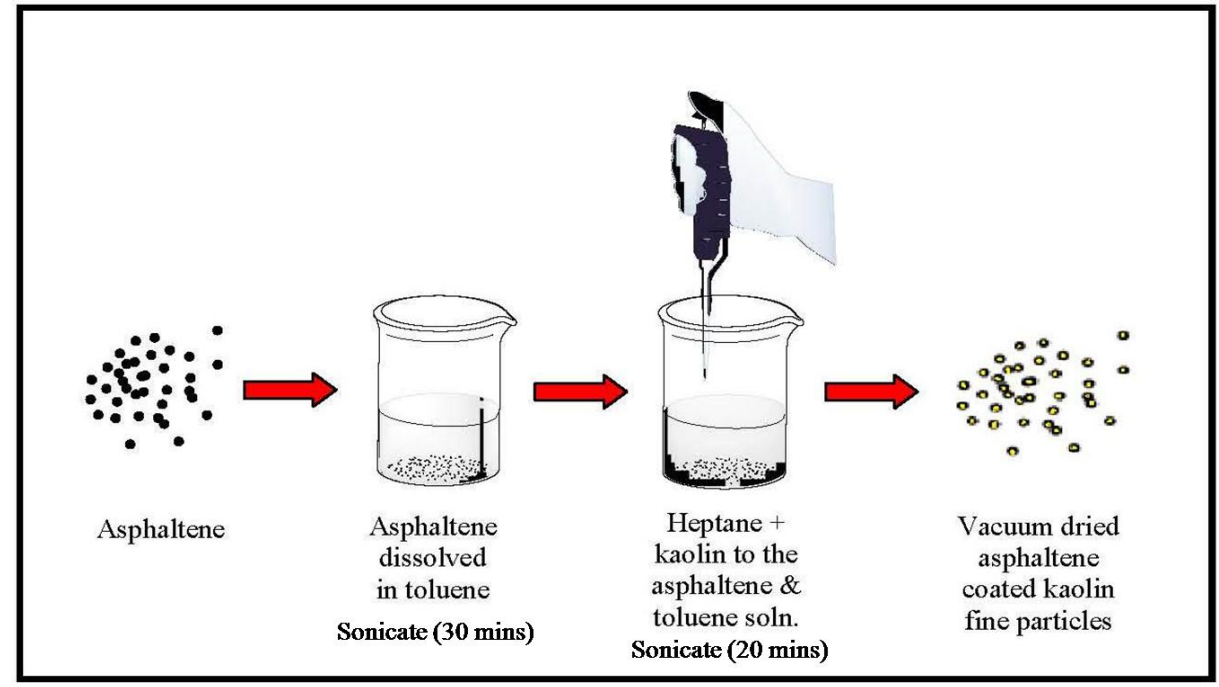


Figure 3.3 Schematic for asphaltene coated kaolin (model fines) synthesis

3.7 Design of Experiments

For both the phases 1 and 2, Central Composite Design methodology was used to design the experiments. For phase 1, 3 independent variables were chosen as the impacting process parameters. The effects of pressure (1200, 1300 and 1400 psig), temperature (355, 365 and 375 °C) and particle loading (1, 1.25 and 1.5 g) on kaolin deposition was studied and the design of experiments used for phase 1 is shown in Table 3.1. Out of 20, 6 experimental runs were performed under repeated conditions to check the reproducibility of the experimental results. The repeated runs were performed under 1300 psig, 365 °C and 1250 mg particles loading as the reaction parameters.

For phase 2, the effect of particle size was studied first and then the experiments were designed to study specifically the impact of temperature (355, 365 and 375 °C) and pressure (1200, 1300 and 1400 psig). The experimental values used to perform hydrotreating in this phase a presented in Table 3.2 For all the experiments in this phase, the particle loading was kept constant (1 g). Similar to Phase 1, the experiments at the centre points were again checked for reproducibility as obtained from the software. While weighing the fine particles before suspending them into the LGO feed, an error of ±0.002 mg was considered.

3.8 Hydrotreating

The feed was filtered through 0.22μm Millipore filter to ensure there were no fine particles present in the feed; so as to have proper model fines study. The hydrotreating of the LGO feed was carried out in a 450 ml vessel of a batch reactor. 200 ml of LGO was mixed with 0.8-1.6 g kaolin using a magnetic stirrer for 30 minutes to obtain fines suspended LGO feed. With the ideal amount of fines in the feed (~100 ppm) it was not possible to study the impact of process parameters. Hence the concentration of fines was taken higher after consulting the available literature (Wang et al.,1999). Wang et.al., 1999, took 0.97-0.98 g of kaolin in ca. 240 g of oil. The purpose was to get fast accumulation of fines on the catalyst bed during the study.

The reactor was properly sealed with split rings and then the slip ring (See Figure 3.1). Following this, the reactor temperature was slowly ramped for hydrotreating (355-375 °C) based on the design of experiments for both phases 1 and 2 of the study (see Tables 3.1 & 3.2). After the temperature was stable at the set point, the reactor was pressurized from 1200-1400 psig using hydrogen, as specified in the design of experiment. The agitation speed of the reactor was set to 750 rpm and the reaction time was set to 8 h. At the eighth hour the oil product sample was collected in a 2 ml vial to determine the catalyst activity in terms of sulfur conversion. The reactor vessel was then left to cool and the pressure was vented out when the reactor temperature was ambient.

3.9 Mass Balance

Separating the Fine Particles after Hydrotreating

For mass balance the particles were divided into 3 categories (See Figure 3.4)-

1) Fine particles suspended in the hydrotreated feed
2) Fine particles that deposited on the reactor assembly, impeller shaft, screens and on the outer walls of the catalyst basket
3) Fine particles that interacted with the catalyst bed.

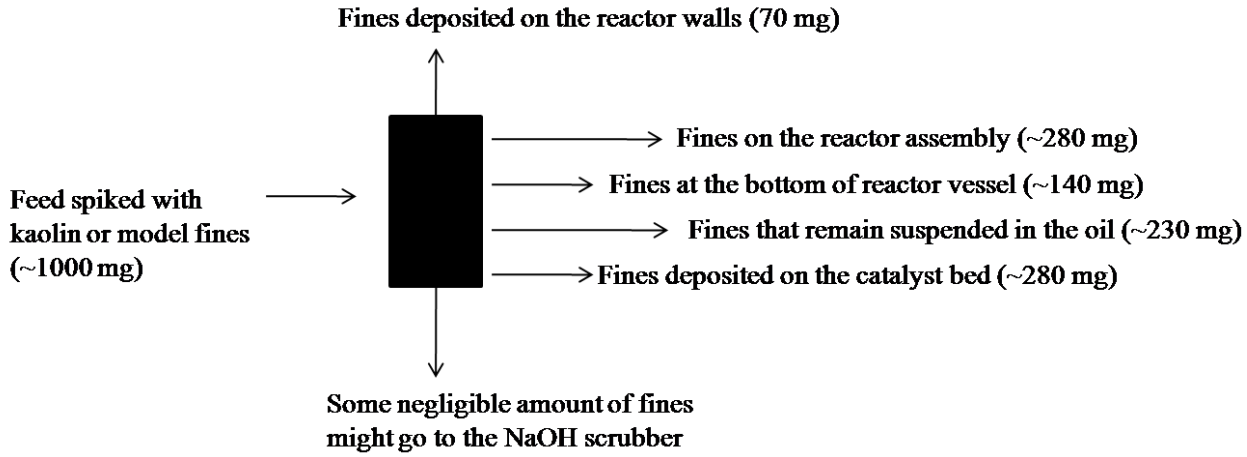


Figure 3.4 Schematic representation of fines deposition during hydrotreating with example

For separating the fines from the feed, the feed was filtered through 0.22µm membrane filter using a buchner funnel. Filtrate was twice passed through the filter to ensure all fines were collected on the filter paper. Fine particles were seen to deposit on the filter in the form of black mass.

In case of fines that were deposited on the reactor assembly, all the reactor parts including the impeller, outer screen and mesh of the catalyst basket and the fines on the walls of the vessel were washed with hexane and the dripping hexane was collected in a beaker. The reactor assembly was then carefully detached and sonicated in hexane to ensure all fines were recovered. The hexane containing traces of dissolved feed oil and fine particles was then filtered through 0.22µm membrane filter using a buchner funnel. The filtrate was twice passed through the filter to ensure all fines were collected on the filter paper. The fines that were not recovered from the feed and from the reactor assembly were assumed to be deposited on the catalyst bed, as it was a closed system used in this study (Appendix A).

Drying the Fines

The membrane filters with black mass (containing fine particles) deposited on them were placed in a petri-dish and the filter paper was then dried in a vacuum oven at 70 °C for 24 h to

remove all the volatiles. The dried black mass was weighed. A similar procedure was followed to weigh the black mass after each experiment.

CHNS of the Fine Particles

The deposited black mass on the reactor assembly and the catalyst basket contained fines, carbon, hydrogen, nitrogen and sulfur from the oil. Therefore, the amount of carbon, nitrogen and sulfur present in the black mass was determined from CHNS analysis and was subtracted from the total weight of the sample to determine the weight of fine particles (kaolin). Hydrogen balance was not included as kaolin does contain hydrogen. For carbon balance, the following equation was used-

$$\mathbf{C_{dep} = (C_{\%}/100)*(Wt_{total}/ C_{sample})} \qquad \mathbf{(3.1)}$$

Where,

C_{dep} = Total carbon in the deposited sample
$C_{\%}$ = % carbon in deposition detected in CHNS analysis
Wt_{total} = Total weight of the deposition
C_{sample} = Weight of the sample for CHNS

Similarly, the nitrogen and sulfur balance was carried out.

3.10 Catalyst Regeneration Study

Regeneration study for the spent catalyst with deposited fines was conducted to check if the catalyst is chemically affected due to fines deposition. Each run was repeated thrice to account for reproducibility. First the catalyst was used in a hydrotreating reaction for a feed without fines suspended in it. The catalytic activity was recorded in terms of sulfur conversion. Further another hydrotreating reaction was conducted to treat model fines suspended feed. After the reaction the spent catalyst with fines deposited on it was sonicated for 2 hours in hexane and reused for hydrotreating the feed without fines. For all the runs, the process conditions were maintained constant and are presented in Chapter 5.

Table 3.1 Design of experiments for Phase 1 (kaolin spiked feed)

Exp No.	Pressure (±10 psig)	Temperature (±1 °C)	Particle loading (±0.002 mg)
1	1300	348	1250
2	1300	365	1250
3	1300	365	1250
4	1300	365	1670
5	1200	375	1500
6	1300	365	1250
7	1468	365	1250
8	1200	355	1000
9	1300	365	830
10	1132	365	1250
11	1200	375	1000
12	1300	365	1250
13	1300	382	1250
14	1300	365	1250
15	1400	375	1500
16	1300	365	1250
17	1200	355	1500
18	1400	355	1500
19	1400	375	1000
20	1400	355	1000

Table 3.2 Design of experiments for Phase 2 (asphaltene coated kaolin spiked feed)

Exp No.	Pressure (±10 psig)	Temperature (±1 °C)
1	1200	355
2	1441	365
3	1159	365
4	1400	355
5	1400	375
6	1300	365
7	1300	365
8	1200	375
9	1300	365
10	1300	365
11	1300	351
12	1300	365
13	1300	379

3.11 Characterization

ICP-MS

The elemental composition of the catalyst in terms of Ni and Mo was quantified using ICP-MS. 0.1 g of catalyst was dissolved in aqua regia at 150 °C for 8 h and the sample was left overnight at room temperature. When the samples were properly dissolved in the acid solution, the final sample was prepared with 0.2N aqua regia and analyzed with a mass spectrometer.

BET

Nitrogen adsorption- desorption isotherms were studied to obtain the Brunauer-Emmett-Teller pore size, pore volume and surface area of the support and the catalyst samples using micromeritics ASAP 2000 instrument. All the samples (0.2 g) were degassed at 120 °C prior to analysis. The relative pressure within the range of 0.05-0.03 was used to determine the surface area using BET analysis. For pore diameter, pore volume and pore size distribution, Barrett, Joyner, Halenda (BJH) method was used. Total pore volume was determined by determining the nitrogen adsorbed at a relative pressure of 0.95 with an assumption that the external surface adsorption was negligible as compared to the adsorption in the pores.

Fourier Transform Infrared Spectroscopy (FTIR)

PerkinElmer (Wellesley, MA, USA) Spectrum GX instrument equipped with KBr beam splitter and a DTGS detector was used for FTIR analysis. The spectra were collected in the range of 400-4000 cm^{-1} and each spectrum was scanned 32 times. The catalyst sample was crushed to a fine powder and the FTIR analysis was done. The transmittance through the sample was reported.

Scanning Electron Microscopy (SEM)

The surface morphology of the catalyst and deposited kaolin was examined using SU8010 scanning electron microscope, Hitachi, Japan. Scanning was performed at the magnification of 8000, 25,000 and 50,000. The samples were mounted on aluminium slabs with the help of carbon tape. The catalyst samples did not require gold coating to get the images.

X-Ray Fluorescence (XRF)

Synchrotron radiation based spatially resolved X-ray fluorescence (SR-XRF) experiments were carried out at the SXRMB beamline14 of the Canadian Light Source (Saskatoon, Canada) covering the energy range between -450 to 9785 eV. Fluorescence was excited with a monochromatic X-ray beam of 9 keV with a flux of about 1 1010 photons per s. The

fluorescence spectra were recorded with a 4-element Si(Li) detector mounted at 90 relative to the incoming beam. Samples were mounted inside of a vacuum chamber onto a sample manipulator allowing the control of rotation and a movement perpendicular to the X-ray beam.

Elemental Analysis and Carbon Content

The mass fractions of carbon, hydrogen, nitrogen and sulfur in the samples were determined from elemental analysis performed on Vario EL III elemental analyzer (Vario EL III, Elementar, Hanau, Germany). The extracted asphaltene and model fines synthesized in the laboratory were analyzed using this technique.

3.12 Liquid Product Analysis

Nitrogen and sulfur conversions of the untreated and hydrotreated feed was analyzed using N S analyzer. The total nitrogen content of the hydrotreated product was measured using a combustion/chemiluminescence technique (ASTM D4629) and the sulfur content was measured using a combustion/fluorescence technique (ASTM D5463). The concentrations of sulfur and nitrogen were determined using Antek 9000 NS analyzer.

4. Impact of Process Parameters on Kaolin Deposition

In this chapter, the findings from phase 1 where the impact of process parameters on kaolin deposition was studied are reported. The focus of this phase was to understand the individual and combined impact of 3 process parameters (pressure, temperature and particle loading) on kaolin deposition. The physical and chemical changes in the catalyst due to kaolin deposition were also studied. In the beginning of the chapter, results for laboratory synthesized NiMo/γAl_2O_3 catalyst characterization are presented. Following this are the outcomes of the hydrotreating runs and the spent catalyst characterization. The model for bed deposition and sulfur conversion for this phase are also included.

The standard error was within ±2% for sulfur conversion and ±5% for fine particle deposition. The error in fine particle deposition is due to the loss of fine particles incurred while extracting the fines from feed and reactor assembly or while collecting samples for sulfur analysis.

4.1 Catalyst Characterization

4.1.1 Nitrogen Adsorption Desorption Isotherm

The surface areas of the alumina support, synthesized NiMo catalyst and spent catalyst obtained after hydrotreating the oil with and without kaolin were determined using BET method, and the pore size and pore volume were determined using BJH pore size distribution method. The results for the analysis are presented in Table 4.2. It was observed that the surface area, pore volume and pore size of the alumina support decrease as the Ni and Mo metals are impregnated on the support, due to the filling of the pores by the impregnated metals (Yu, Ramanathan, and Oyama 1998). The elemental concentration of Ni and Mo in the synthesized catalyst was determined using ICP-MS (Ferdous et al. 2004). Ni was 2.3 wt% (targeted 2.5 wt%) and Mo concentration was 11 wt% (targeted 13 wt%).

There is a significant decrease in the surface area and pore size of the catalyst after hydrotreating as seen for spent catalyst (Spent NiMo/γAl_2O_3) in Table 4.2. However, no difference in textural properties is observed for spent catalyst generated with and without kaolin in the feed. As clear from the results for catalyst with minimum bed deposition (experiment 9) and maximum bed deposition (experiment 17) in Table 4.2, there was no

variation in the textural properties even when the kaolin deposited on the catalyst bed had a difference of ~500 mg (see Table 4.1). This is because the average particle size (5μm) of kaolin is much larger than the average pore size of the synthesized mesoporous catalyst. Therefore, the presence of kaolin in the feed does not alter the textural properties of the catalyst. Thus, from nitrogen adsorption-desorption isotherm it is clear that the kaolin particles do not settle inside the pores of the catalyst and rather, get adsorbed on the surface.

Table 4.1 Design of experiment, sulfur conversion and bed deposition results

Exp No.	Pressure (psig)	Temperature (°C)	Particle loading (mg)	Activity (wt% Sulfur removal)	Bed Deposition (mg)
1	1300	348	1250	43.1 ±2	247.8 ±5
2	1300	365	1250	63.9 ±2	278.9 ±5
3	1300	365	1250	61.1 ±2	287.4 ±5
4	1300	365	1670	55.2 ±2	479.1 ±5
5	1200	375	1500	63.5 ±2	307.8 ±5
6	1300	365	1250	60.4 ±2	293.1 ±5
7	1468	365	1250	64.1 ±2	251.7 ±5
8	1200	355	1000	41.5 ±2	220.5 ±5
9	1300	365	830	61.2 ±2	46.1 ±5
10	1132	365	1250	58.5 ±2	157.8 ±5
11	1200	375	1000	65.6 ±2	189.9 ±5
12	1300	365	1250	63.6 ±2	288.0 ±5
13	1300	382	1250	66.2 ±2	289.6 ±5
14	1300	365	1250	61.8 ±2	276.2 ±5
15	1400	375	1500	69.7 ±2	383.3 ±5
16	1300	365	1250	63.4 ±2	281.0 ±5
17	1200	355	1500	47.7 ±2	598.2 ±5
18	1400	355	1500	43.1 ±2	247.8 ±5
19	1400	375	1000	63.9 ±2	278.9 ±5
20	1400	355	1000	61.1 ±2	287.4 ±5

Table 4.2 BET results obtained to study the textural properties of the catalyst

Sample	**Surface Area** (m^2/g)	**Pore Volume** (cm^3/g)	**Average Pore Diameter** (nm)
Alumina Support	279	0.81	11.3
NiMo/γAl_2O_3 Cat	236	0.48	8.1
Spent NiMo/γAl_2O_3	164	0.29	6.8
Spent NiMo/γAl_2O_3 minimum fines (Exp 9)	160	0.29	6.9
Spent NiMo/γAl_2O_3 maximum fines (Exp 17)	157	0.27	6.9

4.1.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy was used to derive information of the functional groups present in the catalyst samples. Figure 4.1 shows the FTIR spectra of different catalytic samples; the spectra of the fresh catalyst, spent catalyst and spent catalyst in kaolin suspended feed were named fresh, spent and spent K, respectively. The peak at 1100 cm^{-1}, which was present in all three samples, was due to Al-O stretching of alumina (Ferdous, Dalai, and Adjaye 2004b; Palcheva et al. 2012). The metal peaks at 469 cm^{-1}, 538 cm^{-1} and 754 cm^{-1} are due to the presence of Si-O, Al-O-Si and Si-O-Si vibrations, respectively (Grill et al.,2009; Saikia et al.,2003). These peaks were found only in the catalyst that was used for hydrotreating the kaolin suspended LGO feed. As kaolin is alumino-silicate, the presence of these peaks in the spectrum of the spent catalyst with kaolin (spent K) sample determines the presence of the kaolin deposits on the catalyst. Thus, it can be inferred that the kaolin present in the feed interacts with the catalyst. The presence of a peak at 1450 cm^{-1} and at 1456 cm^{-1} for the spent catalyst (spent) and the spent catalyst with kaolin (spent K) deposit is for C-H bending (Grill et al.,2009). These peaks are due to the presence of hydrocarbons on the catalyst after hydrotreating reaction.

The FTIR spectra in Figure 4.2 is for the black deposit collected from the top screen of the catalyst basket, as shown in the photograph beside Figure 4.2, and the commercial kaolin sample. Both the samples have similar peaks except for the additional peaks at 2927 cm^{-1} and 2873 cm^{-1} and these occur due to the $C\text{-}H_3$ stretching and the one at 1360 cm^{-1} is due to Si-CH_2-Si vibrations (Mgbemena et al.,2013). This shows that the kaolin that comprises of Si interacts with the C. Thus, the black deposit on the reactor assembly and on the catalyst basket was found to be kaolin with some carbon particles.

4.2 Kaolin Interaction Study with Catalyst/Bed

4.2.1 Catalyst Activity for Feed with Different Concentration of Model Fines

It can be observed from Table 4.1 that the maximum sulfur conversion was achieved at higher temperature. For example, in experiment 15 with 375 °C temperature, the sulfur conversion was maximum (69.7%). All the reactions at this temperature had high sulfur conversion (63%-69%), regardless of pressure and particle loading, as seen in Table 4.1 for experiments 5, 11, 15 and 19. It can be inferred that temperature impacts sulfur conversion as an independent variable. On comparing the impact of pressure, from Table 4.1, it can be seen

that if particle loading and temperature remained the same, there was an increase in sulfur conversion with increasing pressure. For example, with process conditions 1200 psig, 355 °C, 1500 mg (experiment 17), the sulfur conversion was 47.7% and with process conditions 1400 psig, 355 °C, 1500 mg (experiment 18), the sulfur conversion was higher (53.8%). Similar results were observed at 1200 psig, 375 °C, 1500 mg (experiment 5); the sulfur conversion was 63.5% and for experiment 15 at same temperature and particle loading but with higher pressure (1400 psig), the conversion was higher (69.7%).

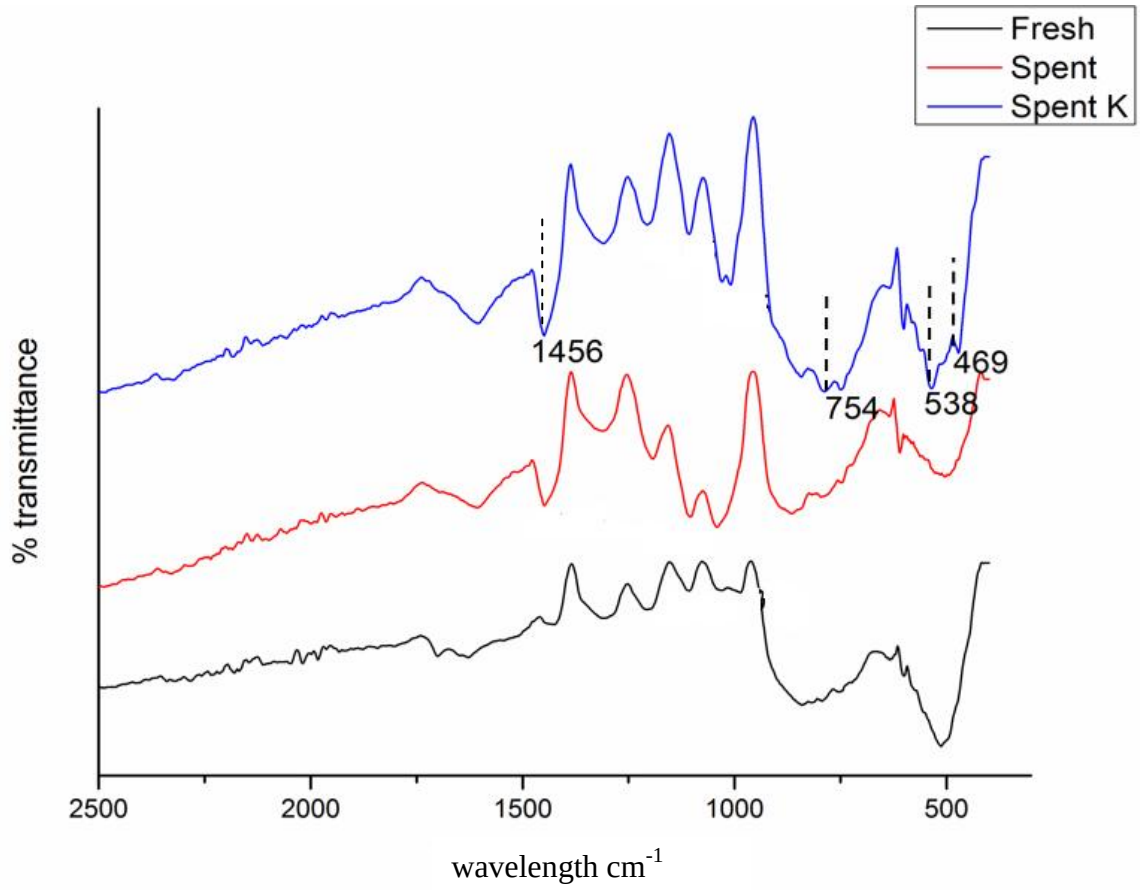


Figure 4.1 Fourier Transform Infrared Spectroscopy of the fresh catalyst (Fresh), spent catalyst after hydrotreating reaction (Spent) and Spent catalyst after hydrotreating kaolin suspended LGO feed (Spent K)

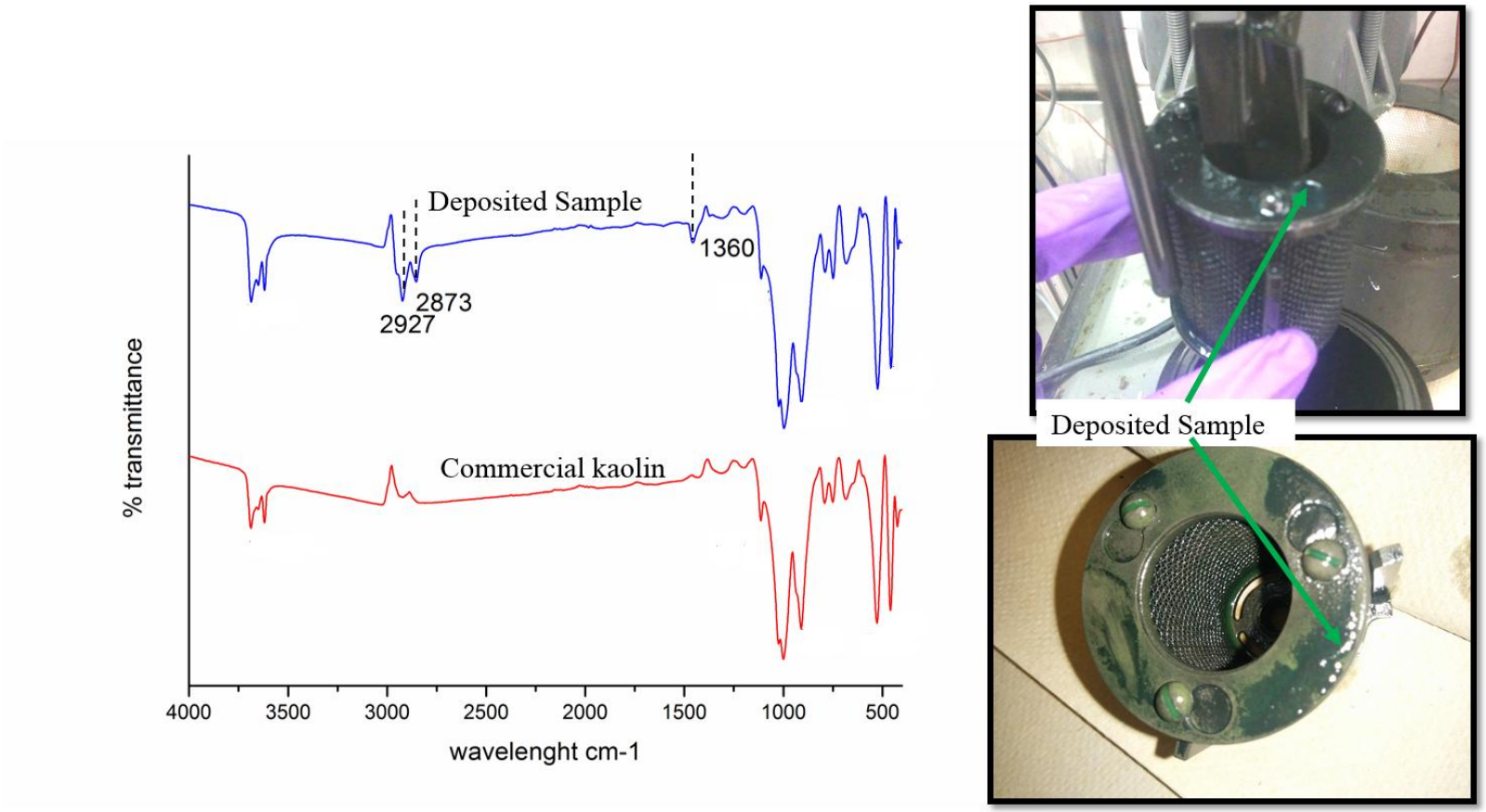


Figure 4.2 Fourier Transform Infrared Spectroscopy of commercial kaolin (Kaolin), and the black deposit on the catalyst basket after hydrotreating reaction (Deposited sample)

Thus, high pressure led to higher sulfur conversion. Variation in particle loading, on contrary, did not impact sulfur conversions. In case of particle loading of 1000 mg in experiment 20 (1400 psig, 355 °C), the sulfur conversion was 51.9%; which was close to 53.8% obtained for experiment 18 with particle loading 1500 mg (1400 psig, 355 °C). From these results, it could be inferred that variation in particle loading did not impact the sulfur conversion of the feed.
Bed deposition, on contrary, showed some irregularities. When mass balance results for deposition at various conditions of process parameters were compared, it was difficult to predict which parameter impacted the bed deposition most (see Table 4.1). Hence, it was difficult to predict the most important process parameter affecting bed deposition without statistical analysis. Therefore, a detailed statistical analysis was undertaken for an accurate study of the responses to the process parameter. This was performed on the acquired data and the results are discussed in section 4.4 of this chapter.

4.2.2. Macroscopic Images for Particle Deposition in the Reactor

After hydrotreating the LGO feed, the reactor vessel containing oil was removed and photographs of the catalyst basket were taken after washing it carefully with hexane to remove oil and get a clear picture of the deposited fines. The images of the catalyst basket were collected after every experimental run and a significant amount of kaolin was seen on the screens and mesh of the basket (see Figure 4.3). The images of the basket showed the major amount of kaolin contributing to the fine particles deposited on the reactor assembly. These images were supported with the mass balance results for bed deposition shown in Table 1. If the amount of fines deposited for a particular experimental run is maximum for the reactor assembly, the amount deposited on the catalyst would be least; as the total fines in the system can be accounted from the following equation-

$$\mathbf{K = FR + FO + FB} \qquad \mathbf{(4.1)}$$

where;

K= Total kaolin added to the feed, FR= fines deposited on the reactor assembly, FO= fines suspended in the oil, and FB = fines on the catalyst bed.

Hence, if the value of FR was more, then the value of FB would be less, as the value of FO is found to be more or less the same from the mass balance studies. The same trend is seen in the photographs of the catalyst basket collected. Figure 4.3 shows images of the catalyst basket after three different experimental runs. The basket had least deposited fines on it in

case of experiment 17 (1200 psig, 355 °C, 1500 mg) and the maximum deposit was seen in case of experiment 9 (1300 psig, 365 °C, 830 mg). These results were further supported by the mass balance results, where the maximum bed deposit was found in case of experiment 17, which had minimum deposit on the top screen of the catalyst basket. As inferred by the FTIR results (Figure 4.2), these black deposits comprised of kaolin particles and hydrocarbons.

4.2.3. Mass Balance

The carbon, nitrogen and sulfur content of the deposited particles were measured using CHNS analyzer. For FR and FO collected fines the carbon, nitrogen and sulfur mass were subtracted from the sample's weight to get the accurate amount of kaolin recovered. As the experiments were run in a closed system, it was assumed that whatever amount of fines was not present in the treated feed and on the reactor assembly was deposited on the catalyst bed. Table 1 shows the bed deposition of the kaolin particles calculated from mass balance results for all 20 runs. The mass balance calculations showed that the maximum fines were deposited on the catalyst for experiment 17 (1200 psig, 355 °C, 1500 mg) and the minimum deposition of fines on the catalyst bed occurred for experiment 9 (1300 psig, 365 °C, 830 mg).

4.2.4. Scanning Electron Microscopy

Scanning electron microscope was used to study the surface morphology of the catalyst. After the mass balance results, catalysts from different experiments were studied under the SEM. 10 images at different locations of the catalyst pellet were collected for spent catalyst from each experimental run. The SEM images of spent catalyst from experiment 9 (minimum kaolin deposition) and experiment 17 (maximum kaolin deposition) are reported in Figure 4.4. The SEM image of the catalyst from experiment resulting in maximum kaolin deposition (Exp. 17) showed large non-uniform clusters of kaolin deposited on the surface (Figure 4.4 a), catalyst sample from experiment resulting in minimum kaolin deposition (Exp. 9) showed small stacking of the kaolin particles (Figure 4.4 b), whereas, catalyst samples from experiment 12 (moderate kaolin deposition) showed uniform stacking of intermediate size. Thus, the SEM results were well in accordance with the bed deposition results (Table 4.1) calculated using mass balance. Similar results were obtained for other catalysts too.

On comparing the deposition results obtained by mass balance and SEM for sulfur conversion, there was no trend observed. For experiment 9 with minimum (46 mg) kaolin deposit, the sulfur conversion was 61.2%, and in case of experiment 12 (288 mg kaolin deposited) the sulfur conversion was 63.6%. For experiment 17 with maximum (598 mg) kaolin deposited, the sulfur conversion was least (47.7%). Therefore, a constant trend cannot be observed for the impact of bed deposition on sulfur conversion. The decreased conversion in experiment 17 (1200 psig, 355 °C, 1500mg) could be due to the low reaction temperature used in the experiment 17 (see Table 4.1), and it cannot be quantitatively analyzed if the feed conversion was affected by bed deposition. However, there was slight decrease (~5%) in the sulfur conversion when kaolin was added to the feed LGO as compared to that observed in hydrotreating the feed without kaolin at the same conditions (see Table 4.3).

A separate study was also conducted to see the variation in particle deposition on the catalyst surface using SEM with all other parameters being same (pressure was 1300 psig, kaolin particle loading was 1 g) but at 3 different temperatures 355 °C, 365 °C and 375 °C. The images for all three catalyst samples are shown in Figure 4.5. It was found that the maximum deposition occurred in case of maximum temperature and the deposition decreased with decreasing temperature. Thus, temperature was seen to have a major impact on the deposition of fine particles. Catalytic activity was also studied for these three experiments using NS analyzer (Table 4.3). The results showed higher conversion at higher temperature.

4.3 Impact of Presence of Fines on Catalytic Activity

The performance of the synthesized NiMo tri-lobed catalyst was evaluated on the basis of hydrodesulfurization (HDS), calculated as percent conversion (Ferdous et al. 2007). The removal of sulfur is specifically desired by the industry to meet the environmental regulations for eco-friendly emission of the consumed fuel (Botchwey et al. 2004). Therefore, the impact of process parameters on sulfur removal is discussed in detail. When LGO feed was hydtrotreated (1300 psig, 365 °C, without particle loading) the conversion was ~71% for 3 repeated runs (see Table 4.3). However, when 1000 mg of kaolin was added to the feed and hydrotreating was carried out in a batch reactor, the sulfur conversion decreased to ~68% for 3 repeated runs (See Table 4.3). All other conditions were maintained the same apart from the spiking of the LGO feed with kaolin. This showed that there was a slight decrease (~3%) in

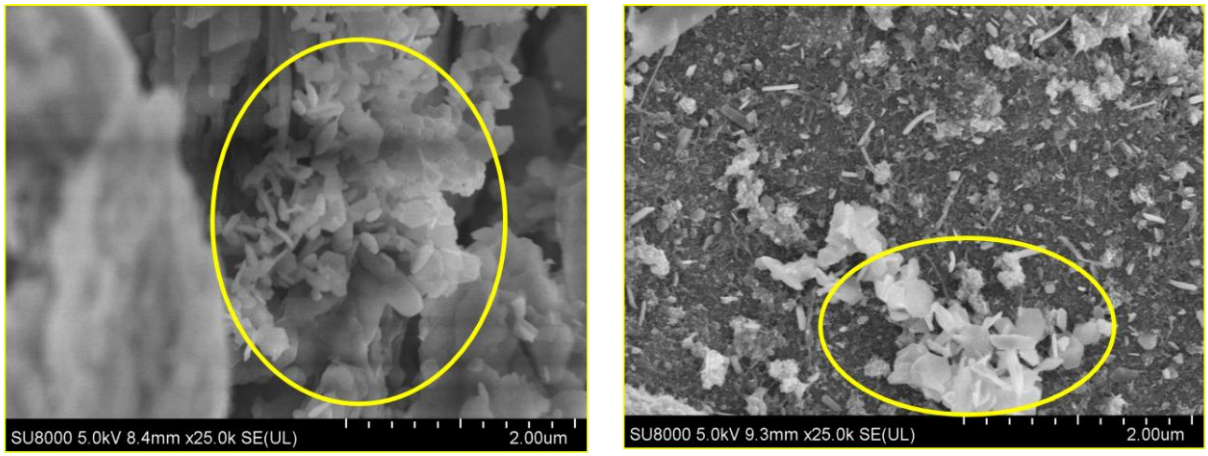
the sulphur conversion due to the presence of fine particles. This could be due to the blocking of the active sites of the catalyst as a consequence of kaolin deposition.

Moderate deposition on catalyst basket (Exp.12)

Minimum deposition on catalyst basket (Exp.17)

Maximum deposition on catalyst basket (Exp.9)

Figure 4.3 Photographs of the catalyst basket taken after the reaction run as described in Table 1 for Exp. 12 (1300 psig, 365 °C, 1250 mg), Exp. 17 (1200 psig, 355 °C, 1500 mg) and Exp. 9 (1300 psig, 365 °C, 830 mg)



Spent catalyst Exp. 17 (maximum fines deposition)

Spent catalyst Exp. 9 (minimum fines deposition)

Figure 4.4 SEM images of the catalyst with kaolin deposited after Exp. 17 (maximum agglomeration), and Exp. 9 (minimum deposition).

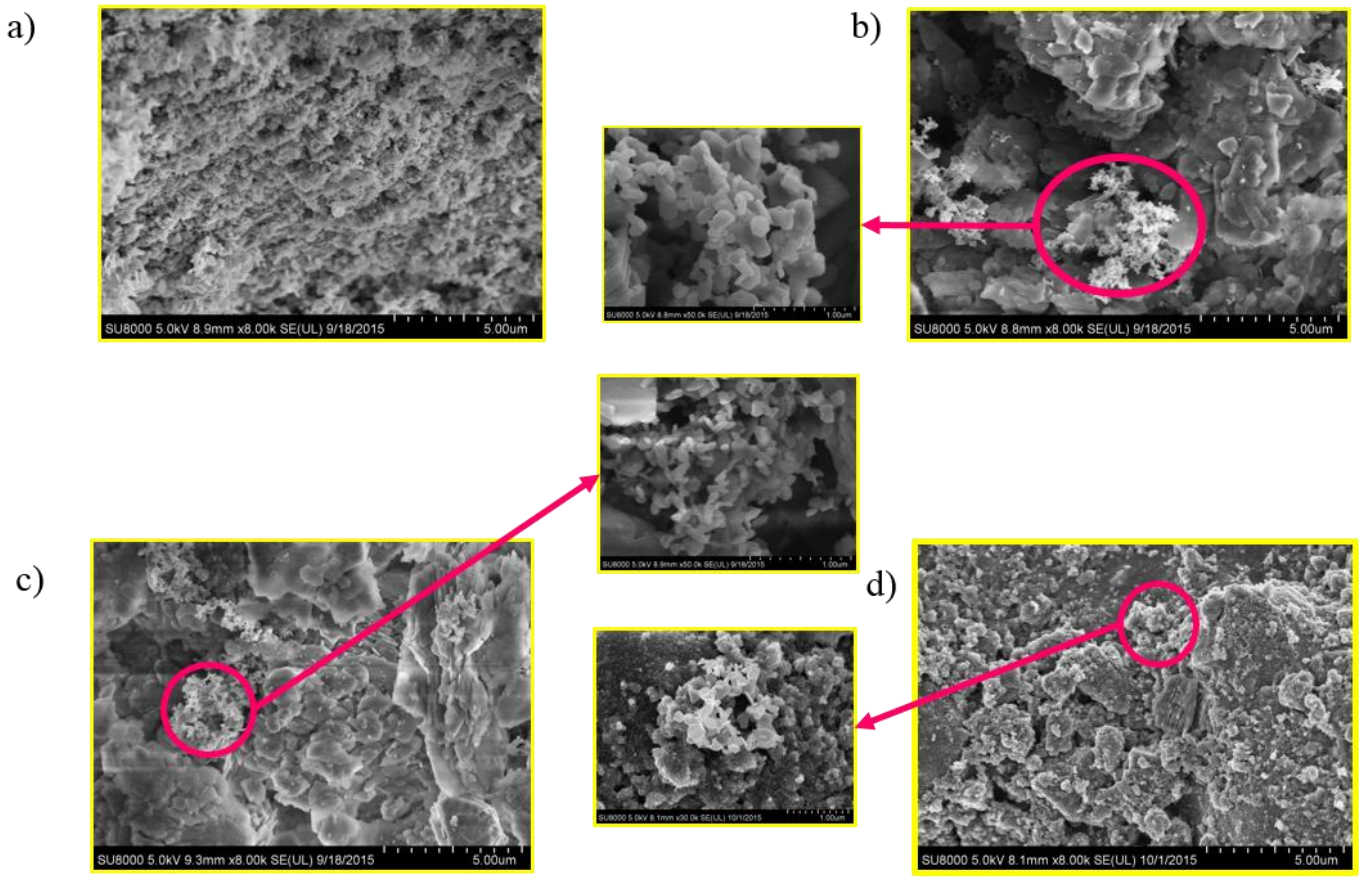


Figure 4.5 SEM images for effect of temperature study a) Spent catalyst; Spent catalyst with kaolin deposited at – (b)375°C, (c) 365°C, (d) 355°C

Table 4.3 Effect of temperature on sulfur conversion

Exp No.	Temperature (°C)	Pressure (psig)	RPM	Particle loading (mg)	Sulfur Conversion (wt%)	Bed Deposition (mg)
1	355	1300	750	1000	60 ± 2	93.7
2	365	1300	750	1000	68 ± 2	116.2
3	375	1300	750	1000	74 ± 2	144.0
4	365	1300	750	0	71 ± 2	0

Table 4.4 Lack-of-fit and R-squared statistics for different models fitted to the data

Best Fit Model	Terms in model	Eliminated effects	p-value for lack of fit	R-squared
Bed deposition	P, T, PL, P*P, PL*PL, P*T	T*T, P*PL,T*PL	0.126	0.74
S conversion	P, T,PL, T*T, PL*PL	P*P, P*T, P*PL, T*PL	0.111	0.92

T- Temperature; P-Pressure, PL- Particle Loading

Table 4.5 Response optimization of the results for the developed model

Optimization No.	Particle loading (g)	Temperature (°C)	Pressure (psig)	Target Bed deposition (mg)	Target Sulfur conversion (wt%)
1	1.6	360	1450	100	60
2	0.8	364	1380	100	60

4.4 Statistical Analysis and Modeling

Due to the combined effects of the process parameters it is difficult to predict the data and obtain a trend without using a statistical tool. Hence, the trends for bed deposition and sulfur conversion were studied using central composite design tool so as to understand the individual and combined impact of process parameters. The objective was to interpret the data and understand the trend to obtain models for sulfur conversion and bed deposition for feeds with variable particle loadings. Also, with the help of the statistical analysis, the optimized values of temperature and pressure for minimum bed deposition without impacting the sulfur conversion were targeted to achieve. The details of the statistical study and the results obtained are further discussed in this section.

4.4.1 Data Normality

It is essential to examine the normality of the data points before building a model to understand if the data acquired is significant to construct a model. If the data are normal then they lie close to the straight line on the probability plot. This means that the data acquired fits the process and can be held significant. Where the acquired data is not normalized, box cox transformation is commonly employed as a statistical tool to normalize it. The normality of both the sulfur conversion and that of bed deposition was tested by the probability curve; the probability curve for sulfur conversion fell sufficiently close to the straight line with a p-value of 0.009 which suggests that the data clearly follows normal distribution. However, in case of bed deposition curve, the value of p was 0.99. This suggests that the data points for bed deposition do not follow a normal distribution on the probability plot and hence box cox technique is used on the acquired data in this case.

4.4.2 Model Construction

When the data were used to develop a model in its raw form the value of R square was considerably less. Hence, the normalized data that was given by the software after box cox transformation was used to get higher value for R-square and a satisfying p-value for the lack of fit test. The lack of fit test and the R-squared statistics acquired from the analysis of the best fit model for both, bed deposition and sulfur conversion, are shown in Table 4.4.

The appropriateness of the model can be depicted by the lack of fit test (Kang et al. 2015). The overall variability of the observations that can be successfully explained by the model is given by the R^2 value. The p-value for the lack of fit test of sulfur conversion was 0.11 and that of bed deposition was 0.13; which means that the hypothesis that the model might not be well-fitted does not hold good and the predicted model adequately accounts for the acquired data. In case of sulfur conversion the R square is 0.92 which means the model holds good for the responses. The R square for bed deposition is 0.74.

The generalized equation that can be derived by the coefficients in the model for sulfur conversion (SC) and bed deposition (BD) can be expressed as follows-

$$\mathbf{SC^2 = -398372 + 2.618\ P + 2073\ T + 6819\ PL - 2.718\ T^2 - 2746\ PL^2} \qquad \mathbf{(4.2)}$$

$$\mathbf{BD^{0.1} = 214 - 0.1692\ P - 0.573\ T + 2.980\ PL + 0.000457\ P*T} \qquad \mathbf{(4.3)}$$

where; SC = sulfur conversion (wt%) ; BD = Bed deposition (830-1670 g) ; P = Pressure (1132-1468 psig); T = Temperature (348-382 °C); PL = Particle loading (g)

The model for sulfur conversion comprises of P (pressure) and T (temperature) as independent terms and this shows that both these variables are significant. However, for bed deposition model the positive coefficient for PL (particle loading) and that for combined effects of P*T (pressure*temperature) shows that these are the key parameters impacting bed deposition.

4.5 Optimization of Process Parameters

4.5.1 Effect of Various Process Parameters and Interactions

The model helps to study the interaction plots of the process parameters. The main effects plots give information on the parameters that have maximum impact on sulfur conversion and bed deposition. Figure 4.6 (a) shows that the sulfur conversion increases with an increase in temperature. However, it is different in case of bed deposition. It is clear that particle loading is having the most significant impact on bed deposition but temperature as well has a significant impact and we see that the bed deposition increases with an increase in temperature (See Figure 4.6 b). But the impact of pressure was difficult to predict from the main effects plot. This could be due to the significance of the combined interaction of temperature and pressure; and temperature being an individual dominant parameter for bed deposition out of the two. The developed model also supported this hypothesis as it eliminated the interaction terms P*PL and T*PL, while retaining the interaction term between temperature and pressure (T*P) as shown in Table 4.4.

The interaction plots for sulfur conversion and bed deposition were also plotted in the software. Figure 8 (a) shows the interaction plots between the process parameters for sulfur conversion. As seen in the first plot of Figure 8 (a), the interaction of temperature with pressure had (~20%) increase in sulfur conversion. The interaction of particle loading with temperature or pressure did not show any considerable impact on sulfur conversion. However, the trend was dissimilar in case of bed deposition. Figure 4.7 (b) shows the interaction plots for bed deposition with all the reaction parameters under study. As predicted by the model and also seen in Figure 4.7 (b), the interaction between pressure and temperature seemed significant for bed deposition. This is supported by elimination of PL*T and PL*P terms from the model and having a p-value of 0.028 for P*T in case of bed deposition model. Thus, we

can count the interaction between temperature and pressure as a significant one for bed deposition.

4.5.2 Optimization of Operating Conditions

The model could be used to optimize the process parameters for bed deposition and sulfur conversion during a hydrotreating reaction. Figure 4.8 shows the contour plots for temperature, pressure and particle loading for both the responses i.e., sulfur conversion and bed deposition. The contour plot for sulfur conversion (See Figure 4.8 a) shows that high temperature and high pressure yield a higher conversion of sulfur. However, particle loading had no influence on sulfur conversion; as seen in the contour plots between temperature and particle loading and pressure and particle loading. In case of bed deposition the contour plot (Figure 4.8 b) suggests that higher temperature and higher particle loading led to higher values of bed deposition. It is seen that the maximum area under <100 mg of bed deposition is on the bottom right in the contour plot between pressure and temperature. Thus, it can be inferred that high pressure and low temperature gave least bed deposition. The response optimizer tool was used to find the optimized conditions for hydrotreating the feed with fine particles. To account for a variety of bitumen-derived feed with different particle loadings, two optimizations were performed at different range of particle loading. For the first optimization the particle loading was considered high, therefore a value of 1600 mg/ 200 ml feed was fixed for particle loading. The second optimization was targeted for least particle loading and hence, the value of 800 mg/ 200 ml of feed was used. The optimized process parameters for the targeted response of sulfur conversion and bed deposition are presented in Table 4.5.

The optimization study indicates that if the particle loading in the feed was increased from 800 mg to 1600 mg / 200 ml of LGO, the reduction in temperature by 4 °C and an increase in pressure by 70 psig will result in same conversion (60%) and bed deposition (100 mg). The extent to which the temperature and pressure should be varied depends on the amount of particle loading in the feed. In this study the values targeted and the temperature and pressure optimized are for a batch reactor. The model developed can be used to give the values of process parameters to get the desired sulfur conversion and bed deposition. If the reaction temperature and pressure are accordingly modified, depending on the concentration of fine particles in the feed, the problem of premature reactor shutdown can probably be solved.

4.6 Discussion

The entrained fines (kaolin) in the bitumen-derived gas oil accumulate in the catalyst bed, and lead to the catalyst fouling and pressure drop in the reactor. At the conception of this study it was hypothesized that there could be a possible range of temperature and pressure that might lead to a reduced bed deposition. Therefore, the impact of hydrotreating process parameters on the deposition of kaolin on catalyst bed was studied to understand the deposition trends.

The results infer that temperature was the most dominant parameter affecting the deposition of fines on the hydrotreating catalyst bed. This can be concluded based on the results obtained in the individual parameter study of temperature (see Table 4.3) and through the main effects plots obtained by statistical analysis (see Figure 4.6 b). Higher temperature led to higher bed deposition, though it enhanced the sulfur conversion. This could be explained assuming that at higher temperature, as the hydrotreating reaction proceeds, the oil and the byproducts formed are miscible and this leads to the formation of an emulsion. Kaolin particles, which are primarily clay, readily interact with this emulsion and deposit on the catalyst bed depending on the reaction conditions (Wang et al., 1999). The cracked hydrocarbons in the oil also link to the kaolin particles as seen in the FTIR study. The peak at 1360 cm^{-1} that appears due to Si-CH_2-Si vibrations suggests this interaction. These interactions could be another relevant reason for more fines deposition at higher temperatures as higher temperature causes more hydrocarbon cracking. Thus, it is essential to optimize the parameters to get a desired sulfur conversion with less fines deposition.

Previous studies suggest that low hydrogen partial pressure can lead to early catalyst deactivation (Iliuta et al.,2003). Also, higher pressure that is statistically shown to deaccelerate the bed deposition in case of feed with high fines concentration might be compensating the pressure drop in the reactor due to catalyst pore plugging. Several studies reported that the pressure drop in a hydrotreater increased with the concentration of the fine particles (Dehkissia et al.,2008) .

In the next chapter, the interaction and deposition of asphaltene coated kaolin is discussed. It is essential to understand how the behavior of kaolin changes when it surface adsorbs asphaltene and what impact it has on bed deposition. Also, at industrial conditions usually the fines that settle on the catalyst are asphaltene coated kaolin. Therefore, a study on the impact of process parameters on the deposition of asphaltene coated kaolin is included in this work and is discussed in the Chapter 5.

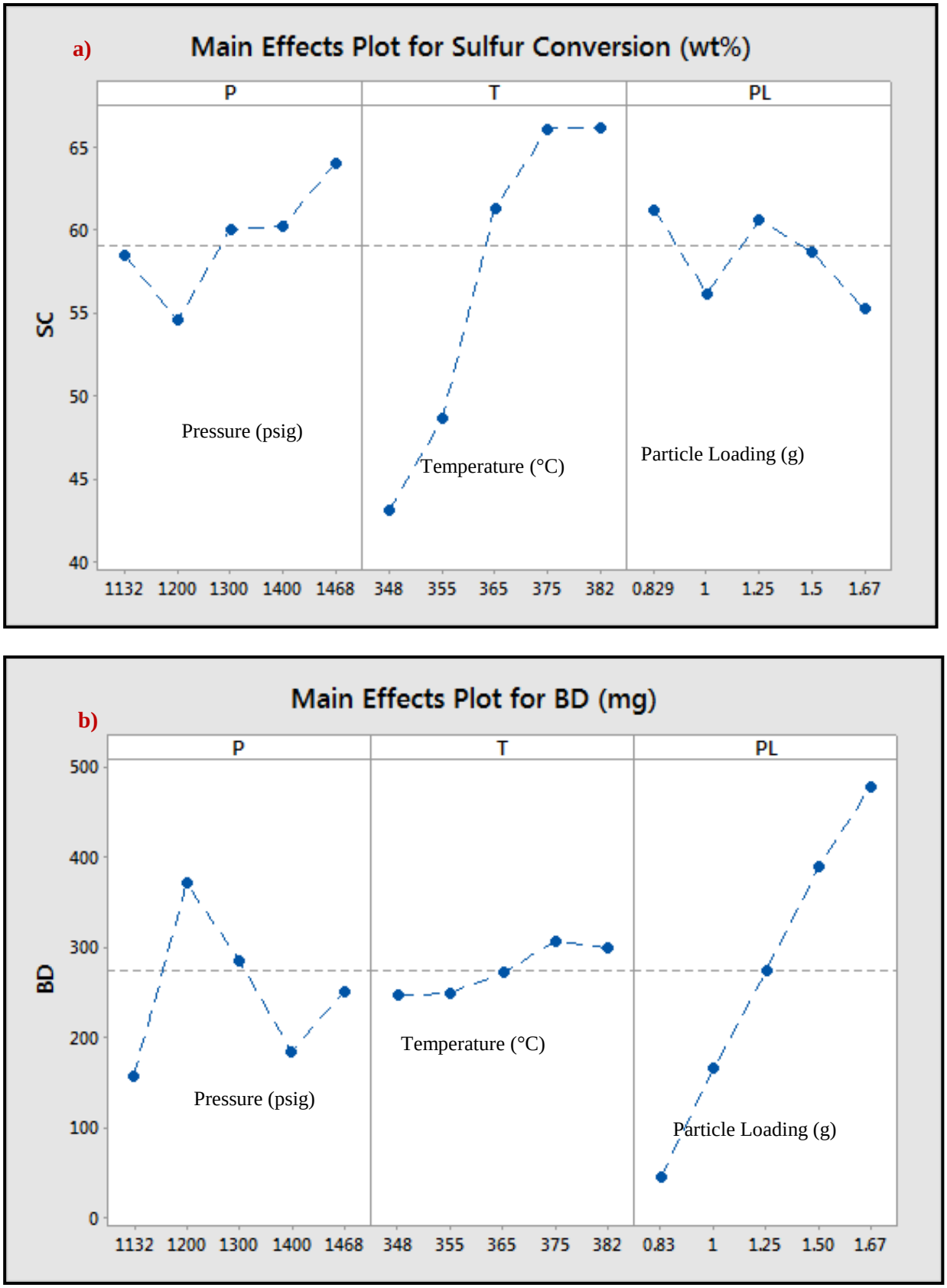
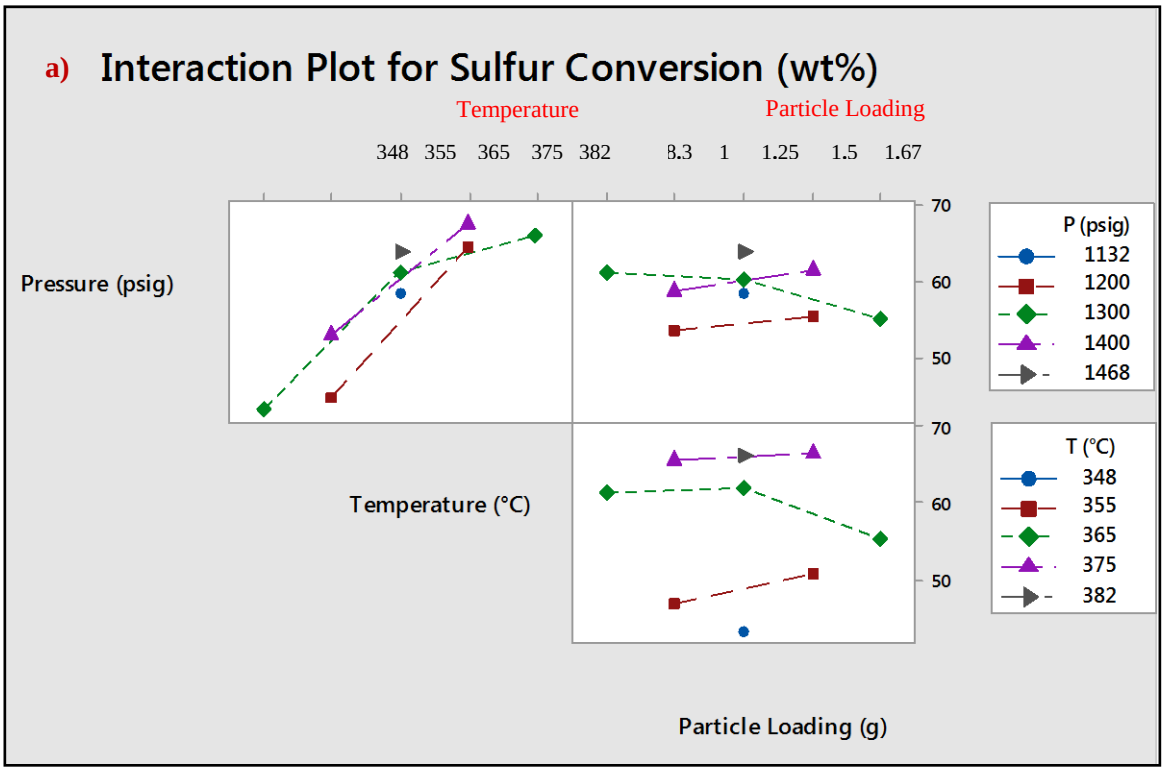


Figure 4.6 Main effects plot for all 3 process parameters P (pressure), T (temperature), and PL (particle loading) obtained from Minitab17 for (a) Sulfur Conversion, (b) Bed Deposition



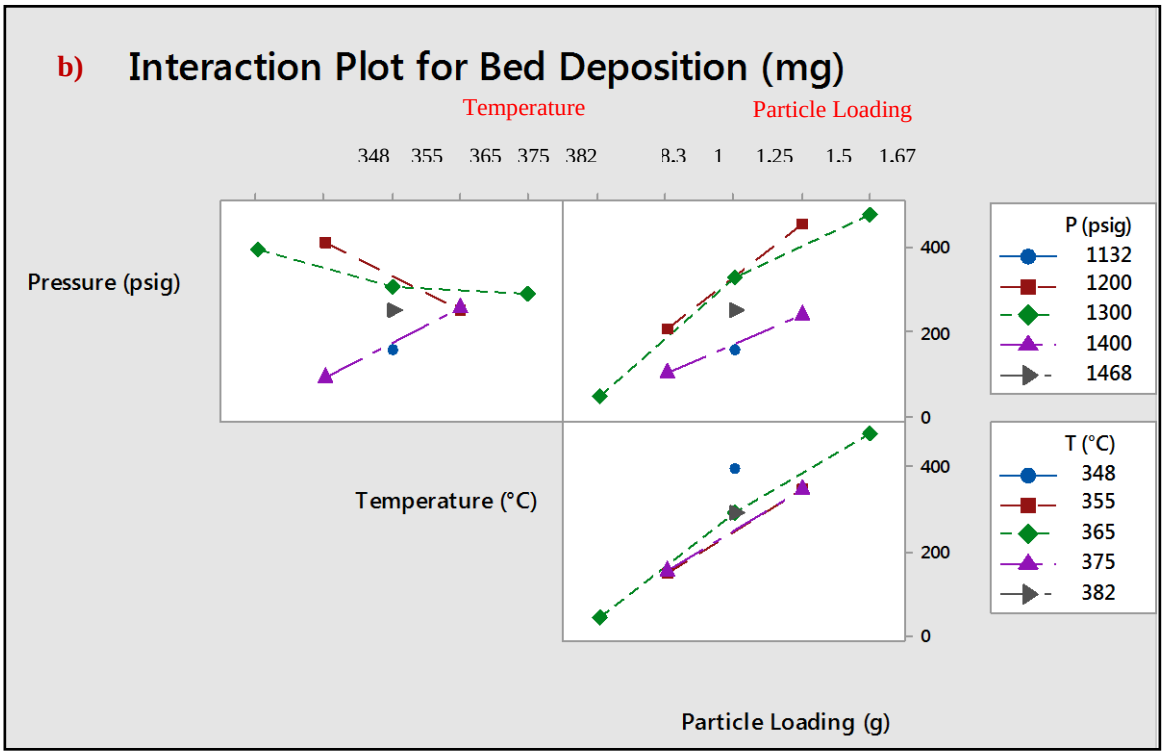
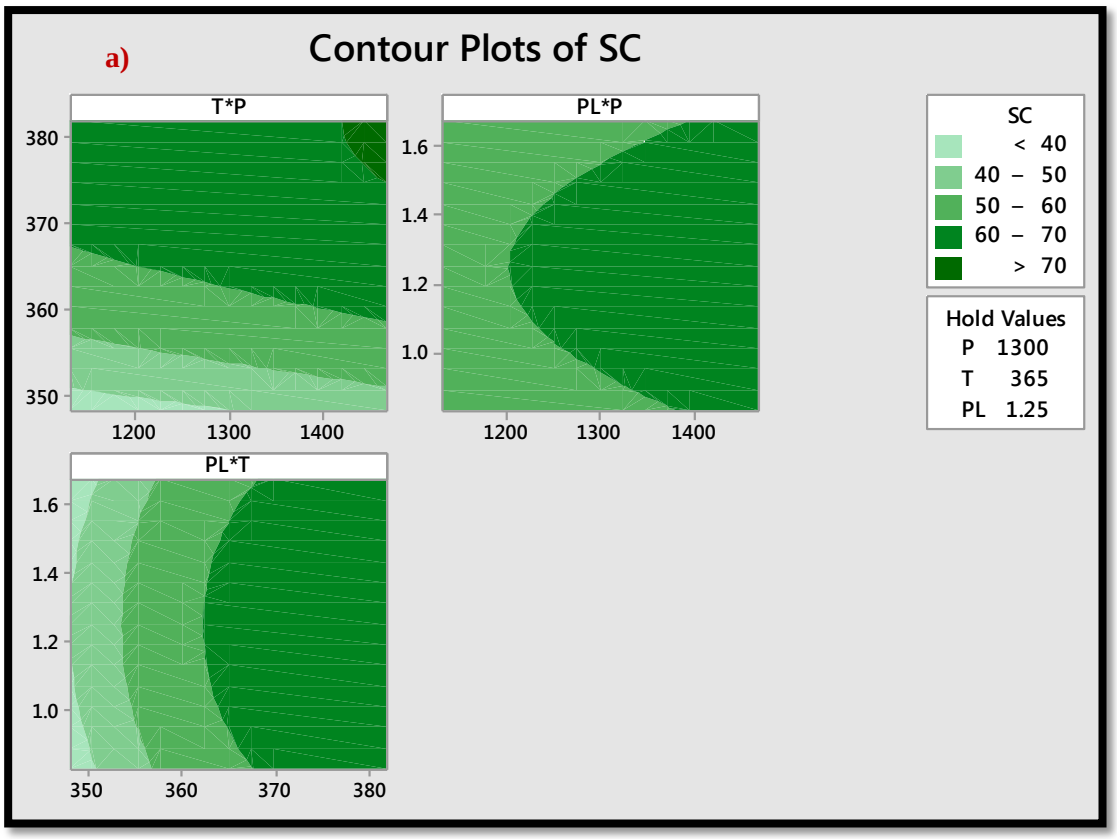


Figure 4.7 Interaction Plots between P (pressure), T (temperature), and PL (particle loading) for (a) SC sulfur conversion (SC), (b) Bed Deposition (BD)



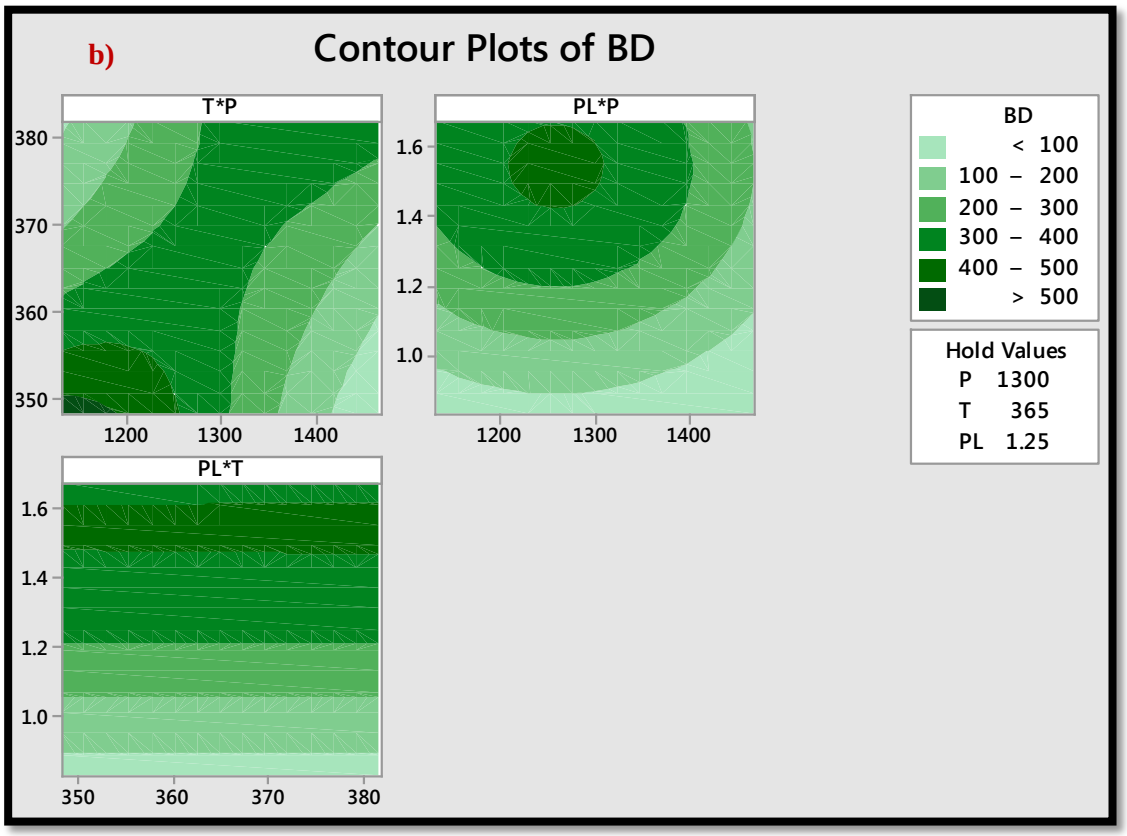


Figure 4.8 Contour plots for response optimization of (a) SC (sulfur conversion), (b) BD (bed deposition)

5. Impact of Process Parameters on Asphaltene Coated Kaolin Deposition

This chapter presents the results for Phase 2, where the individual and combined effects of pressure and temperature on particle (asphaltene coated kaolin) deposition are studied. Apart from the two process parameters studied, the impact of particle size on bed deposition has also been studied. Unlike the previous phase, wherein the particle loading was varied, in this phase the particle loading (1 ±0.03 g) in 200 ml of feed was maintained constant for all the experiments. The standard error was within ±2% for sulfur conversion and ±5% for fine particle deposition. The error in fine particle deposition is due to the loss of fine particles incurred while extracting the fines from feed and reactor assembly or while collecting samples for sulfur analysis. This chapter also includes the discussion related to the effects of temperature and the reaction time study of the deposition of model fines on the catalyst bed.

5.1 Blank Runs

It was essential to understand how the model fines suspended in LGO behave at the reaction conditions, in the absence of the catalyst. To observe the thermal effect on model fines, two separate reactions were conducted at 365 °C. Hydrogen was used at 1300 psig for the reaction and the catalyst basket was packed as in all other experiments. However, for these two reactions there was no catalyst packed in the basket. Glass beads and silicon carbide were rather packed to see if there is any bed deposition taking place in the absence of catalyst and also to see any changes in sulfur conversions. The results obtained are shown in Table 5.1 below. It was found that in the absence of the catalyst, there was no fines deposition on the packed bed. Also, there is no change in the sulfur conversions of the feed.

The mass balance showed that in case of kaolin most of the fines remained suspended in the feed even after the run. Whereas, in case of asphaltene coated kaolin, the division of fines between the feed and the reactor assembly was equal. Thus, the mass balance closure between the feed and the reactor assembly was able to account for total fines initially suspended in the feed before the run. Hence, it was concluded that there was negligible deposition in the packed column of the basket. This was further supported by the images of the glass beads pre and post run which showed no deposition (see Appendix B).

Following conclusions could be drawn from the thermal effect study-

- The presence of catalyst is necessary for sulfur conversion of the LGO.
- In the absence of catalyst there is negligible bed deposition observed.
- Temperature does not impact bed deposition of the fines in the absence of the catalyst.
- The thermal effect study for kaolin and asphaltene coated kaolin was similar except for a slight increase in the deposition on reactor assembly in latter case.

Table 5.1 Blank run results for fines spiked feed

Exp No.	Temperature (°C)	Pressure (psig)	RPM	Particle Size (μm)	Sulfur Conversion (wt%)	Fines in feed post reaction (mg)	Fines on reactor assembly post reaction (mg)
1	365	1300	750	4-6	0	783	211
2	365	1300	750	4-6	0	521	468

Note: The fines loading was 1000 mg/ 200 ml of LGO feed; Exp. 1 was with kaolin spiked feed and Exp. 2 was with asphaltene coated kaolin spiked feed. 6 mg in Exp. 1 and 11 mg in Exp. 2 was assumed to be the negligible amount on the catalyst bed.

5.2 Reaction Time Study

The impact of reaction time on particle deposition was studied at three reaction times (3, 5 and 8 h) keeping all other process conditions same (1300 psig, 365 °C, 1 g). The reactions were carried out at an agitation speed of 750 rpm and the catalyst loading was 1000 ± 0.03 mg. The bed deposition and sulfur conversion results for the reactions at 3 different times are shown in Table 5.2. It was observed that the increase in reaction time led to an increase in the bed deposition as well as sulfur conversion. Increase in reaction time leads to an increase in sulfur conversion; as the reaction proceeds with time the catalytic activity stabilizes and gives higher sulfur conversion. For bed deposition when the reaction time increases, more and more fines come in contact with the catalyst and this causes an increase in bed deposition with time. The chemical interaction between the catalyst and deposited fines is the initial step for kaolin deposition on the catalyst. Asphaltene coated on kaolin desorbs at the reaction conditions and this is where Si in the alumina silicates (kaolin) interacts with the catalyst. The deposition in the industrial reactor occurs till the bed ‘ripens’ where it is completely clogged with deposited fines (Narayan et al. 1997b).

Table 5.2 Effect of reaction time on bed deposition and sulfur conversion

Exp. No.	Reaction time	Fines loading (mg)	Sulfur conversion (wt%)	Bed deposition (mg)
1.	3 h	1000	38	77
2.	5 h	1000	51	129
3.	8 h	1000	69	215

5.3 Effect of Particle Size on Bed Deposition

To study the impact of particle size on fines deposition on the catalyst, two sizes of the fines were tailored in the laboratory. The smaller fines were in the size range of 4-6 μm and the larger ones were as large as ~11 μm. Fines of each size were suspended in LGO and the fines entrained feed was hydrotreated at three different temperatures (355, 365 and 375 °C). Thus, the impact of particle size as well as temperature was studied. The individual impact of pressure on bed deposition was not studied in this phase as in phase 1 pressure did not have any significant individual impact of bed deposition. However, due to the significant combined impact of pressure and temperature on bed deposition the later experiments were designed for both the process conditions as independent variables.

As seen in Table 5.3, there was more deposition for smaller sized particles. This could be due to a preferential deposition of the large sized particles over the inner mesh of the catalyst basket. Thus, smaller particles gave higher bed deposition as seen in case of particles ranging 4-6 μm. The impact of temperature on asphaltene coated kaolin deposition was similar to kaolin deposition; where bed deposition increased with an increase in temperature. Hence, from this study it was found that smaller particles (4-6 μm) and higher temperature (375 °C) would lead to maximum bed deposition as seen in experiment 3 in Table 5.3.

Table 5.3 Effect of temperature and particle size on sulfur conversion and bed deposition

Exp No.	Temperature (°C)	Pressure (psig)	RPM	Particle Size (μm)	Sulfur Conversion (wt%)	Bed Deposition (mg)
1	355	1300	750	4-6	60 ± 2	245.6
2	365	1300	750	4-6	58 ± 2	257.4
3	375	1300	750	4-6	62 ± 2	626.0
4	355	1300	750	9-11	57 ± 2	137.6
5	365	1300	750	9-11	58 ± 2	149.6
6	375	1300	750	9-11	66± 2	369.3

5.4 Impact of Presence of Fines on Catalytic Activity

As discussed in phase 1, the catalytic activity was high at higher temperature. Therefore, the maximum sufur conversion was obtained at 379 °C as seen for experiment 13 in Table 5.4. Both high temperature and high pressure led to higher sulfur conversion. If we compare sulfur conversion for experiments 1 and 4, the temperature is the same (355 °C) for both the experiments. However, there is approximately 10% increase in sulfur conversion when pressure increases from 1200 to 1400 psig. Similar is the trend for experiments 5 and 8 where the temperature is constant (375 °C) but the increased pressure in experiment 5 results in higher sulfur conversion.

If we compare the sulfur conversion of the feed spiked with kaolin with that of asphaltene coated kaolin, we see that the sulfur conversion decreases in latter case. The reason to this could be the asphaltenes that are present in the feed spiked with asphaltene coated kaolin. Asphaltenes are complex hydrocarbon structures with high agglomerating tendency and these might affect the catalytic activity and thus result in comparatively less sulfur conversion of feed. For kaolin spiked feed hydrotreated at 365 °C, 1300 psig with 1000 mg kaolin, sulfur conversion was 68±2%. When feed spiked with asphaltene coated kaolin was hydrotreated at exactly same process conditions, the sulfur conversion obtained was 52.2±2%.

Table 5.4 Design of experiment, sulfur conversion and bed deposition results

Exp No.	Pressure (psig)	Temperature (°C)	Activity (wt% Sulfur removal)	Bed Deposition (mg)
1.	1200	355	42.3 ±2	64.8 ±5
2.	1441	365	64.7 ±2	132.7 ±5
3.	1159	365	53.3 ±2	135.1 ±5
4.	1400	355	53.6 ±2	42.3 ±5
5.	1400	375	67.7 ±2	57.8 ±5
6.	1300	365	54.7 ±2	54.8 ±5
7.	1300	365	54 ±2	54.8 ±5
8.	1200	375	64 ±2	111.7 ±5
9.	1300	365	54.2 ±2	54.8 ±5
10.	1300	365	54 ±2	54.8 ±5
11.	1300	351	48.6 ±2	27.7 ±5
12.	1300	365	54 ±2	54.8 ±5
13.	1300	379	69.3 ±2	139.6 ±5

5.5 Scanning Electron Microscopy Study

SEM images of the catalyst showed that the particle deposition had a similar trend as that in case of kaolin; where, higher temperature led to more particle deposition and this was well supported by mass balance calculations for bed deposition as seen in Table 5.4. Although the SEM images of several catalyst pellets from the reactions were collected, the ones that show the effects of temperature on bed deposition are presented for instance in this chapter (See Figure 5.1).

Figure 5.1 shows SEM images of the catalyst from the experiments that had minimum, moderate and maximum fines deposition. These were the catalysts collected after conducting the study for the individual impact of temperature on bed deposition. The catalysts scanned were collected from the top and the bottom of the basket. The deposition at the top screen of the basket accounts for cake filtration and the fines deposited at the lower region of the catalyst bed cause deep-bed filtration.

In case of asphaltene coated kaolin fines, the deposition was more at the bottom of the reactor and also at the bottom zone of the catalyst bed. Thus, the images shown in Figure 5.1 are of the catalysts from the lower region of the catalyst basket. At lower temperature, the deposition was scattered and at higher temperature larger agglomerates were observed. As seen in Figure 5.1 (a), the deposition at 355 °C was sparse and scattered. The average deposit size was about 2-4 μm. For higher temperatures 365 °C and 375 °C, agglomerates of fines were formed on the catalyst surface. Nonetheless, the size of the agglomerate was large and due to stacked structure of the deposit it was difficult to predict the size of the deposit precisely. Also, the deposited fines were only kaolin as asphaltene might have got desorbed from kaolin surface at reaction conditions (Wang, 2000).

5.6 Study of Deposition Trends

SEM images of the catalyst were collected from the top and the bottom of the catalyst basket. Figure 5.2 shows a schematic of how the fines deposit on the catalyst and also shows the zones in the basket from where the catalyst for cake filtration and deep-bed filtration were collected. As seen in Figure 5.2, the spent catalyst after hydrotreating turns black. If the feed has fines suspended in it, the black spent catalyst is seen to have some grey deposits. When magnified images of these grey deposits were collected, it was found to be alumina silicates (kaolin). The basket is packed with glass beads on the top and bottom and in the middle is the

catalyst mixed with silicon carbide. The catalyst pellets were collected from the top and from the bottom region of the basket as shown in the Figure 5.2.

The X-ray fluorescence (XRF) study was conducted to quantitatively analyze the difference in the amount of fines deposited in the top and bottom zones of the catalyst basket. Pellets from the top and bottom were separately crushed and XRF spectra were obtained. The comparison between the intensities of the of Si was the basis of determination of fines deposition as Si in alumino silicates was an element that was present only in the fines and was absent in the catalyst and feed composition.

Figure 5.3 shows SEM of asphaltene coated kaolin. As seen in the figure, there were deposits of fines seen on the catalyst from the bottom zone of the reactor. Thus, it can be said that in case of asphaltene coated kaolin the major amount of fines were deposited at the bottom zone of the catalyst bed. Figure 5.4 shows the XRF plot for experiment 3 (see Table 5.4). With the help of XRF the intensities for Si in case of the catalyst from the top zone and bottom zone of the catalyst bed were compared. As seen in the plot, the peak intensity for catalyst pellets collected from the bottom of the catalyst bed was higher (1332) than that from the top zone. Thus, from SEM (Figure 5.3) and XRF (Figure 5.4) the difference in the deposition trends of the fines on the catalyst bed were studied. Similarly, the comparison for cake and deep-bed filtration for experiment 13 was also done (see Figure 5.5). It was interesting to note that the peak intensities for the two, experiments 3 and 13 were close but the intensity was slightly more (225 times) for experiment 13 which had higher fines deposition (~9 mg).

The XRF plot for kaolin and asphaltene coated kaolin was compared. The catalyst pellets were collected from effect of temperature study experiments for Phase 1 with 166 mg bed deposition and for Phase 2 which had 149 mg deposited fines. Both the experiments were done at similar process conditions (1300 psig, 365 °C and 1 g). For Phase 1, the catalysts were tested both for top and bottom of the bed. However, the one at the top gave higher deposition. Similarly, for Phase 2 the catalysts from the top as well as bottom were studied for Si peak intensity. It was seen that noticeable peak intensities were obtained for the catalyst pellets from the top zone in phase 1 and that from bottom zone in Phase 2. Hence, it was found that as reported in literature, in this study as well, kaolin led to cake filtration and the presence of asphaltene coating on kaolin led to deep-bed filtration (Wang et al., 2001).

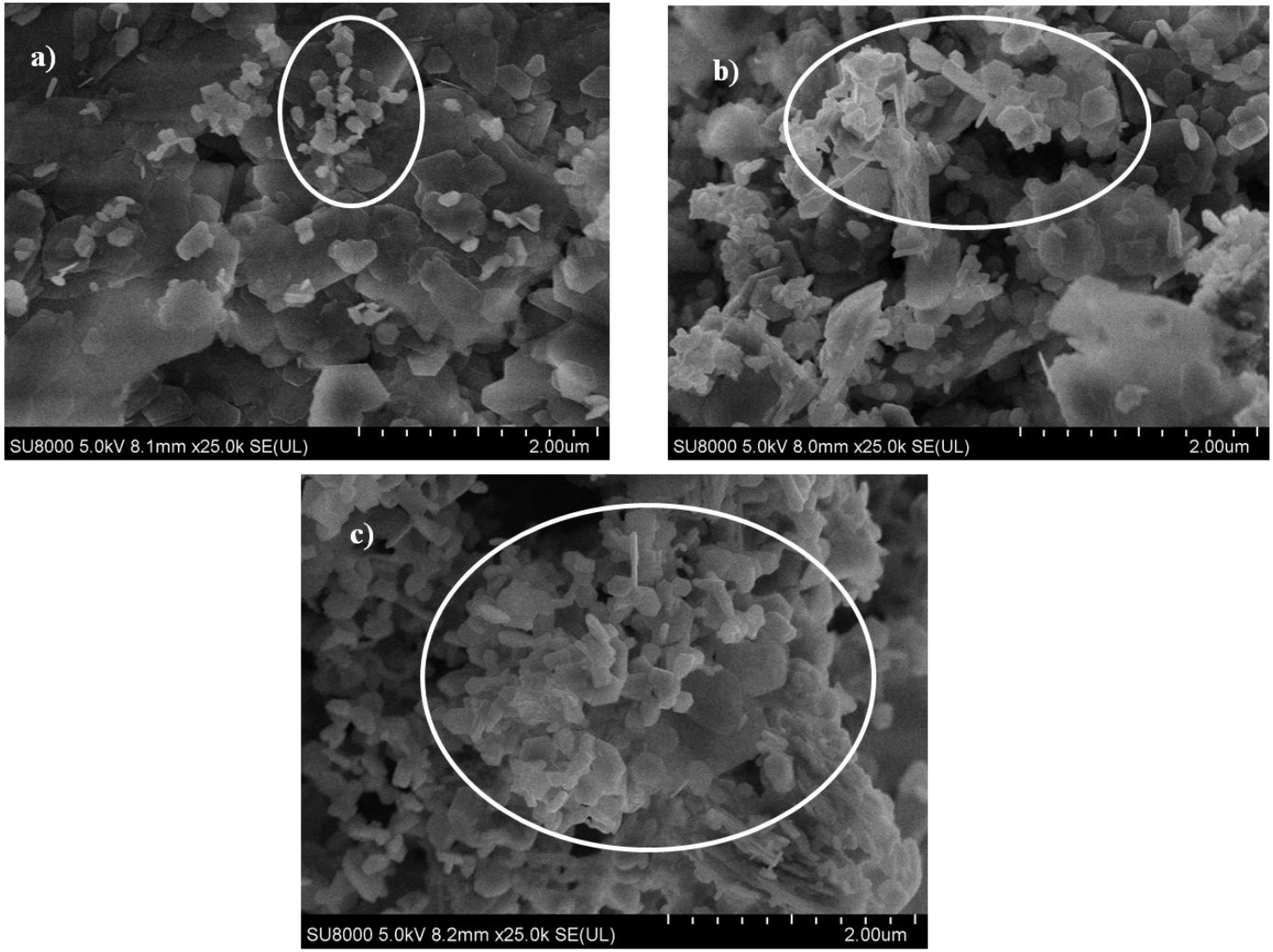


Figure 5.1 Effect of temperature on fines deposition: a) 355, b) 365 and c) 375 ^{o}C with 1 g particle loading (9-11 µm) in 200 ml of LGO

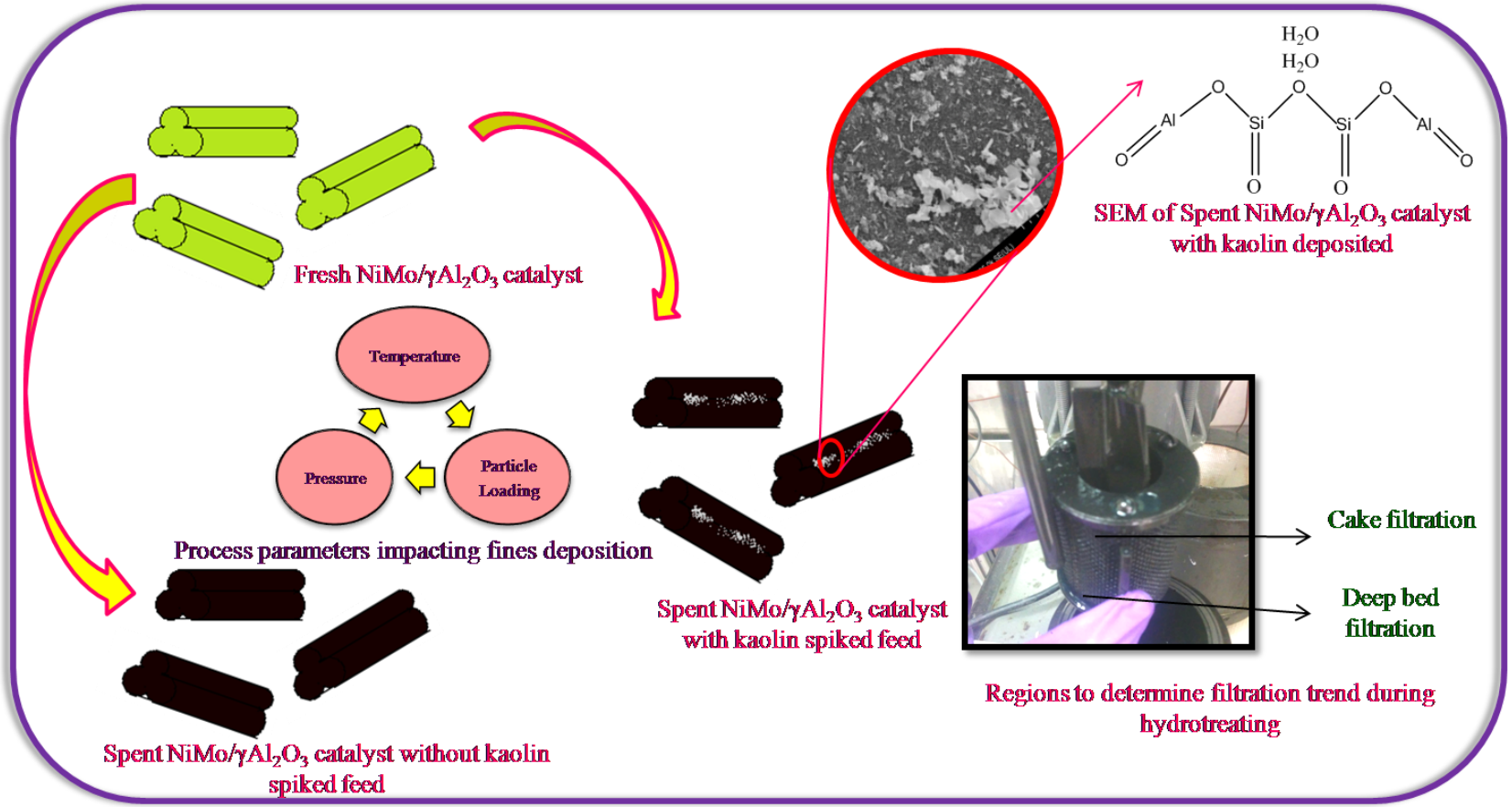


Figure 5.2 Schematic for Fines Deposition on Catalyst

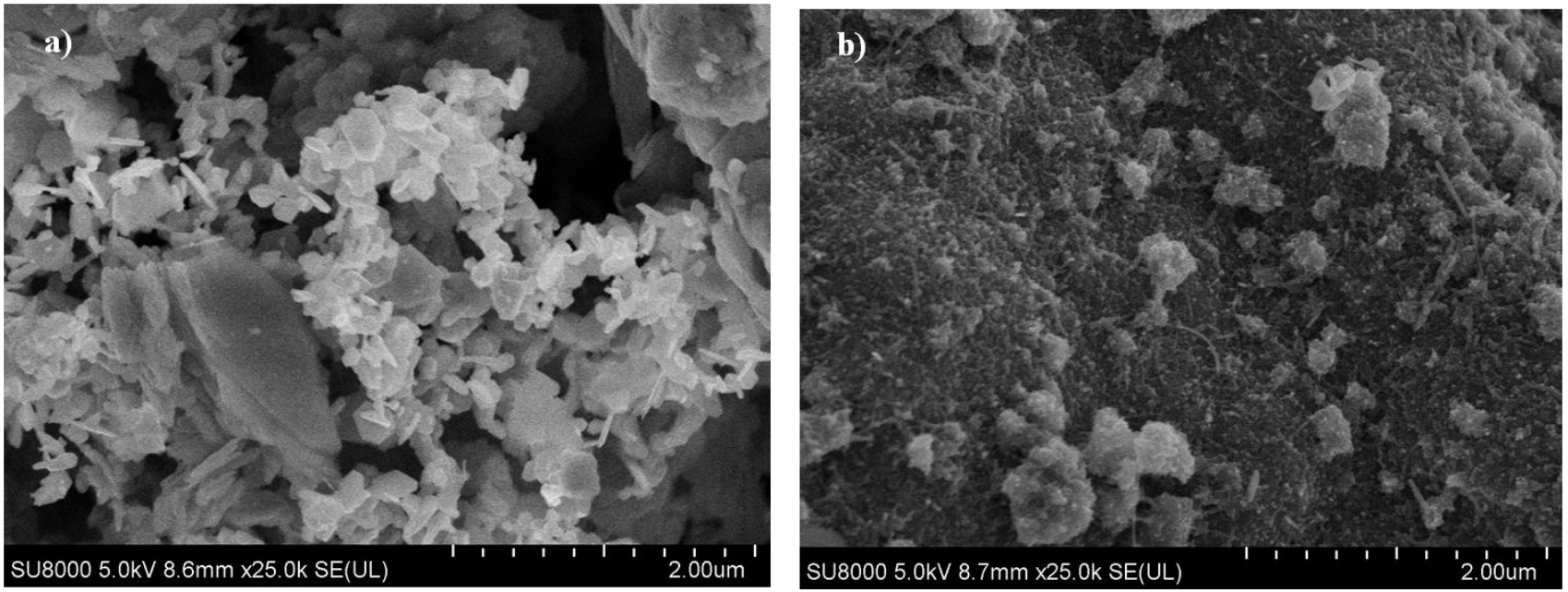


Figure 5.3 Trends of fines (asphaltene coated kaolin) deposition: a) Deep bed filtration, b) Cake filtration

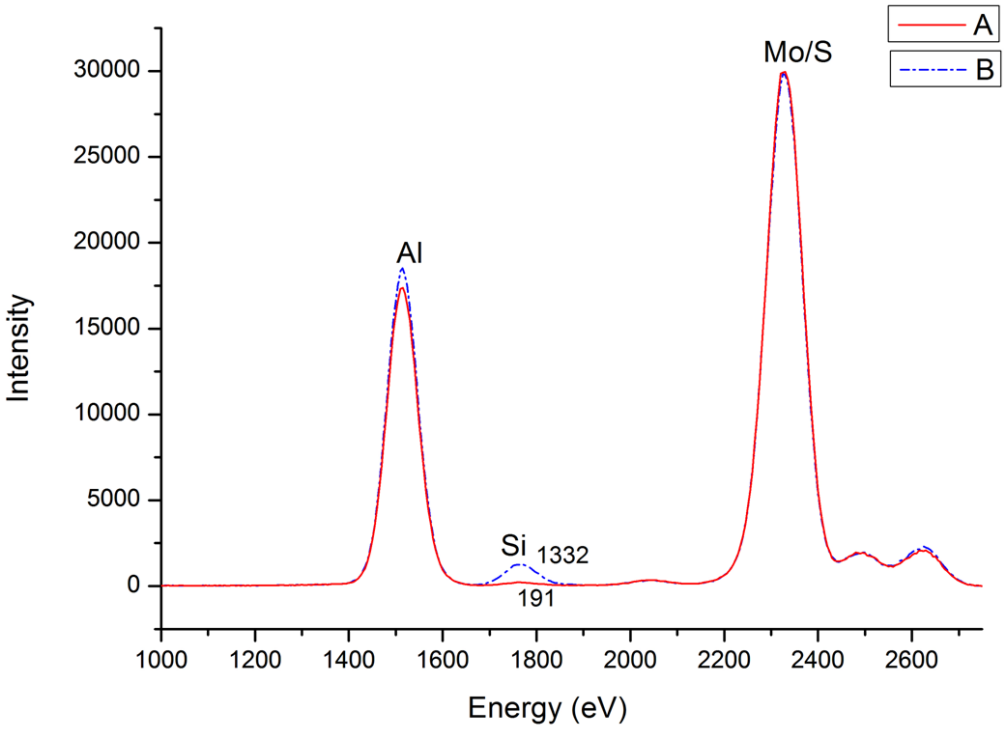


Figure 5.4 XRF plots for fines deposition trend for Exp. 3

A- Spent catalyst with fines deposited (determining cake filtration)
B- Spent catalyst with fines deposited (determining deep-bed filtration)

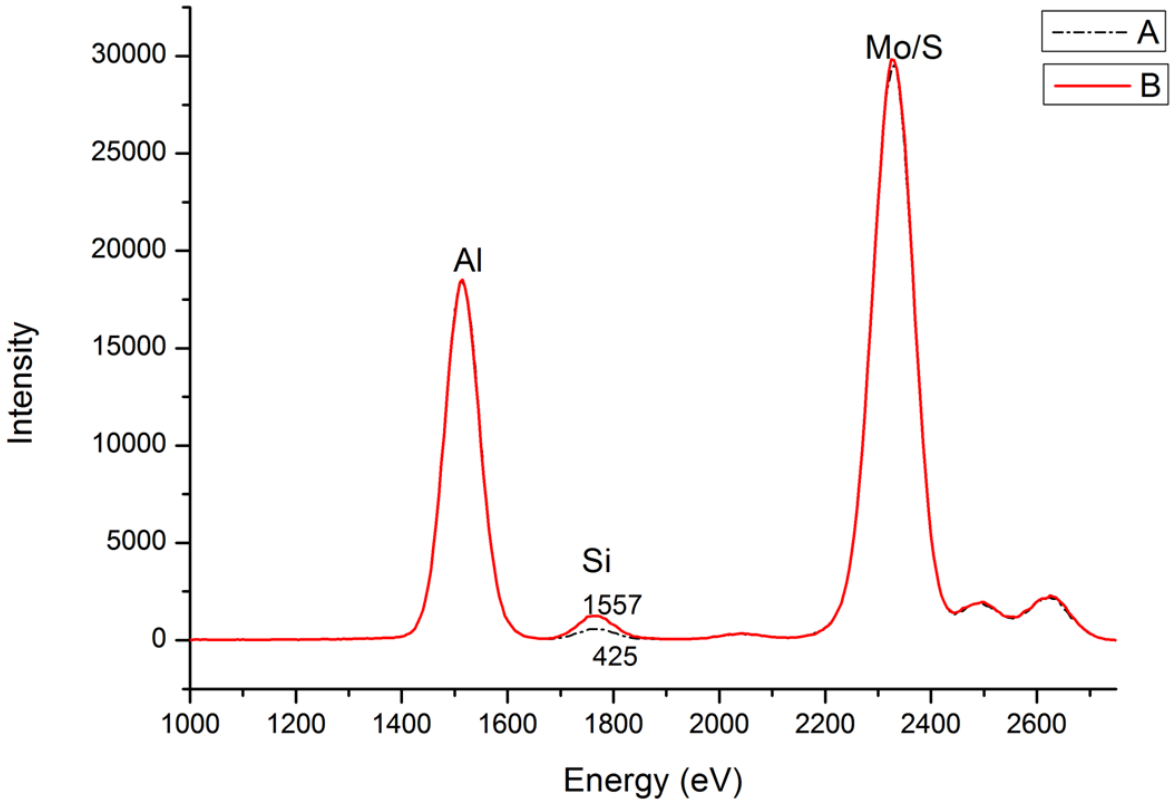


Figure 5.5 XRF plots for fines deposition trend for Exp. 13

A- Spent catalyst with fines deposited (determining cake filtration)
B- Spent catalyst with fines deposited (determining deep-bed filtration)

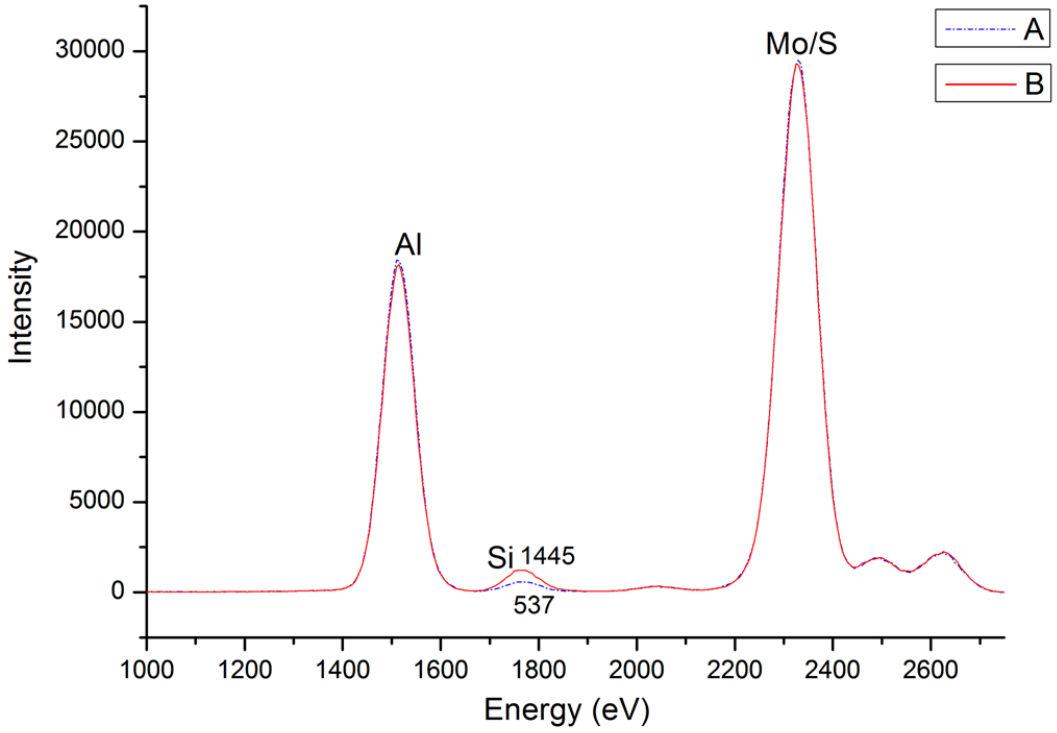


Figure 5.6 XRF plots for fines deposition trend for Phase 1 and Phase 2

A- Spent catalyst with fines deposited determining cake filtration (Phase 2)
B- Spent catalyst with fines deposited determining deep-bed filtration (Phase 1)

5.7 Statistical Analysis and Modeling

As explained in the previous chapter, it is essential to develop the model for sulfur conversion and bed deposition. Through statistical analysis of the acquired data, the effects of temperature and pressure on bed deposition and sulfur conversion were studied. The main effects plots are included and discussed in this chapter to show how each of the process parameters individually impact the fines deposition statistically. The models developed can help in predicting the data values for bed deposition and sulfur conversion at the specified values of temperature and pressure.

5.7.1 Model Construction

The models for sulfur conversion and bed deposition were constructed using CCD statistical tool. The generalized equation that can be derived by the coefficients in the model for sulfur conversion (SC) and bed deposition (BD) can be expressed as follows with variance (R^2) of 0.98 and 0.82, respectively (see Table 5.5). The appropriateness of the model was tested with the help of lack of fit test where the p-value for lack of fit test was 0 for both the models.

$$\mathbf{SC = 1727 - 10.89\ T + 0.218\ P + 0.01943\ T^2 + 0.000199\ P^2 - 0.001908\ T*P} \qquad \mathbf{(5.1)}$$

$$\mathbf{BD^{0.7} = 1053 + 0.528\ T - 1.922\ P + 0.000751\ P^2} \qquad \mathbf{(5.2)}$$

where; SC = Sulfur conversion (wt%) ; BD = Bed deposition (g) ; P = Pressure (1158-1441 psig); T = Temperature (351-379 °C)

As seen from the model both temperature and pressure were relevant for sulfur conversion. However, in case of bed deposition, temperature was a prominent parameter. Also, on comparison the models for bed deposition for kaolin with asphaltene coated kaolin, it is observed that if particle loading is kept constant the P*T combined effect is not relevant in bed deposition model for model fines.

5.8 Optimization of Process Parameters

It is not just statistical model that is important but the optimization of the acquired data as well. In trying to find the optimum process conditions the main effects plots were constructed. As the P*T term was insignificant, the interaction plots between the process variables were not plotted for this study. This shows that the chemistry of the fines significantly dictate the impact of process parameters.

5.8.1 Effect of Various Process Parameters

The process parameters were studied and statistically analyzed. It was found from the main effects plots that individually both temperature and pressure showed clear trends where sulfur conversion increased with an increase in both the process parameters (see Figure 5.7). However, for bed deposition only temperature showed a clear trend for bed deposition. As seen in Figure 5.7 (b) with increase in reaction temperature for hydrotreating, bed deposition increases as well.

5.8.2 Optimization of Operating Conditions

Figure 5.8 shows the contour plots for sulfur conversion and bed deposition to understand the response surface of the dependent variables (bed deposition and sulfur conversion) for the independent variables (pressure and temperature). As seen in the plot, the area under high temperature and low pressure (top right corner) showed maximum sulfur conversion. For bed deposition when temperature was high there was more fines deposition. The values for both the process parameters should either increase or decrease to get minimum or maximum fines deposition.

Further, the process optimization study was carried out for the acquired data. The value for bed deposition and sulfur conversion were fixed to 100 mg and 60% respectively. Bed deposition and sulfur conversion were fixed to the mentioned values so as to optimize the process conditions. If these values were not fixed, the results would give low bed deposition and at the same time lower sulfur conversion too or vice versa. Hence, to get both the data entries optimized it was essential to fix their values to a desired level. The values for temperature were determined using three different values for pressure. The optimization results are shown in Table 5.6. According to the optimization results, with high pressure

(1400 psig) the reactor has to be operated at lower temperature (365 °C) to get the target bed deposition.

Table 5.5 Lack-of-Fit and R-Squared Statistics for Different Models Fitted to the Data

Best Fit Model	Terms in model	Eliminated effects	p-value for lack of fit	R-squared
Bed deposition	P, T,P*P	T*T, P*T	0	0.82
S conversion	P, T, T*T, P*P, T*P	-	0	0.98

T- Temperature; P-Pressure

Table 5.6 Response optimization of the results for the developed model

Optimization No.	Particle size (µm)	Temperature (°C)	Pressure (psig)	Target Bed deposition (mg)	Target Sulfur conversion (wt%)
1	9-11	372	1200	100	60
2	9-11	371	1300	100	60
3	9-11	365	1400	100	60

Particle loading 1000 mg for all readings

5.9 Catalyst Regeneration Study

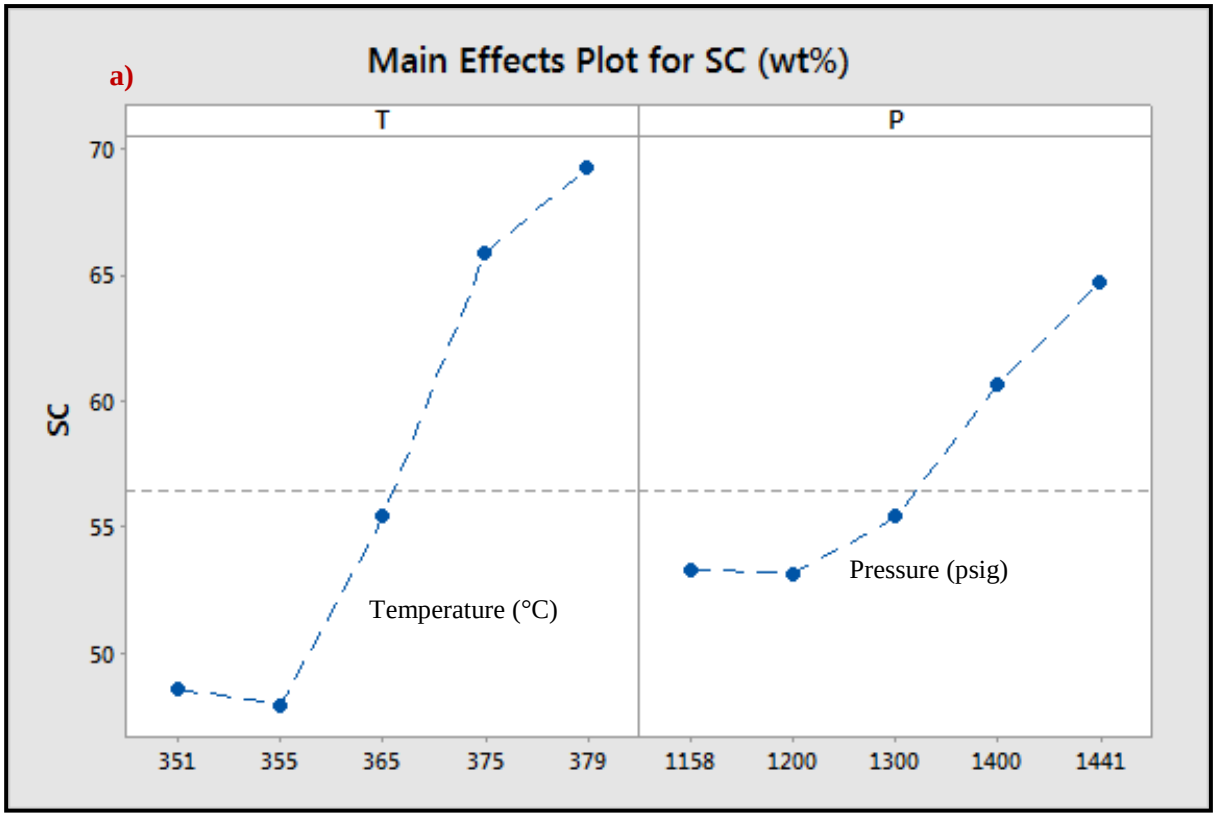
It is seen that the fresh catalyst used in fines spiked feed showed less conversion as compared to the fresh catalyst that was used to hydrotreat the feed without fines. However, it was interesting to see that when the catalyst with deposited fines was sonicated for 2 hours in hexane and reused for hydrotreating the feed without fines, the sulfur conversion was similar to that in case of fresh catalyst used in fines spiked feed (see Table 5.7). The slight variation is probably due to the removal of fines from the catalyst after regeneration process. However, there is not any significant increase in the sulfur conversion which suggests that the fines not only deposit on the catalyst but also interact chemically with it. Hence, even though most of the fines were removed from the catalyst surface, the catalytic activity of the regenerated catalyst did not improve.

5.10 Comparison between Kaolin and Asphaltene Coated Kaolin on Catalyst Performance

Chapters 4 and 5 included the results and discussions describe how two different model fines can have a varied deposition trends. Also, with change in the nature of fines the impact of process parameters changes. There were some relevant comparisons that were discussed in these two chapters and it is interesting to see the difference in the behaviour of the two fines. Table 5.8 provides a summary of the comparisons drawn from Chapter 4 and 5.

Exp No.	Temperature (°C)	Pressure (psig)	RPM	Particle Loading (mg)	Catalyst	Sulfur Conversion (wt%)	Bed Deposition (mg)
1	365	1300	750	1000	Fresh	58 ± 2	238.6
2	365	1300	750	1000	Fresh	58 ± 2	242.1
3	365	1300	750	1000	Fresh	57 ± 2	235.3
4	365	1300	750	0	Fresh	71 ± 2	-
5	365	1300	750	0	Fresh	71 ± 2	-
6	365	1300	750	0	Fresh	71 ± 2	-
7	365	1300	750	0	Regenerated	59 ± 2	-
8	365	1300	750	0	Regenerated	56 ± 2	-
9	365	1300	750	0	Regenerated	59 ± 2	-

Table 5.7 Effect of temperature and particle size on sulfur conversion and bed deposition
Note: The average kaolin size for fines was 9-11 μm



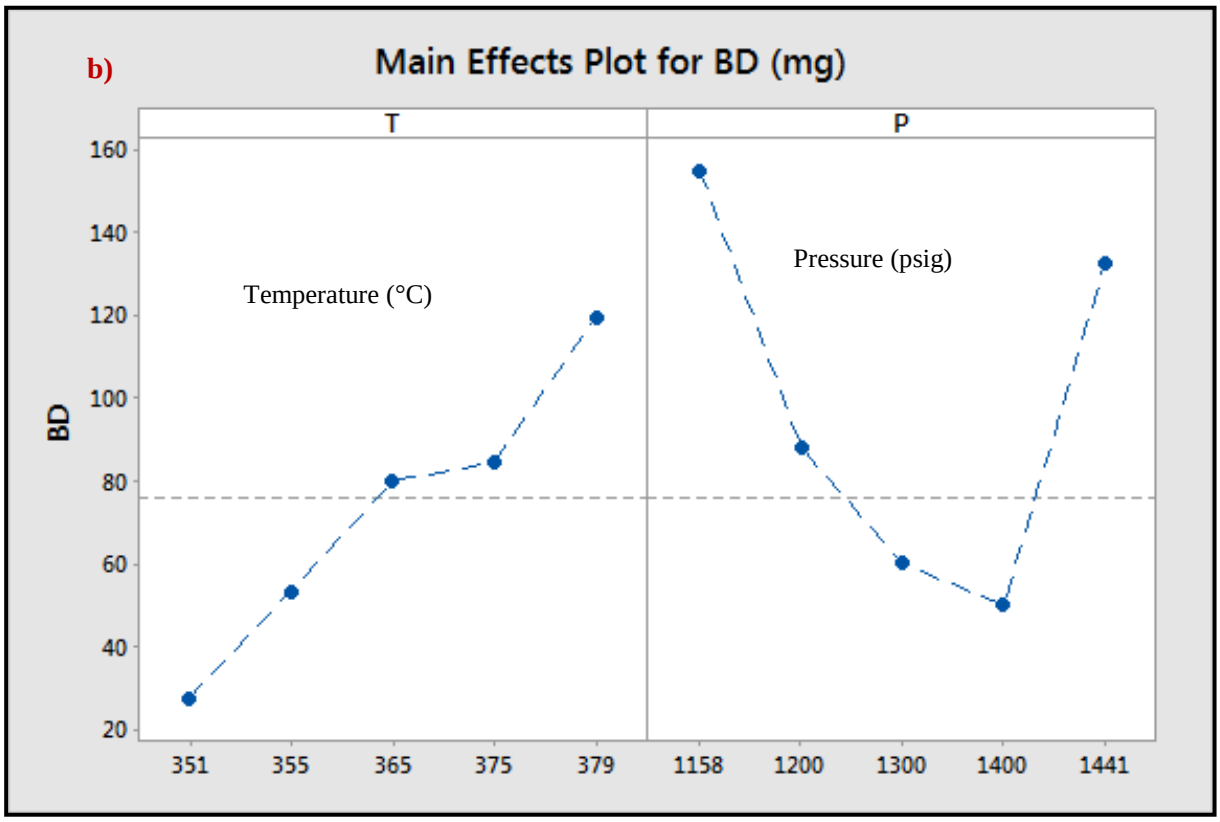


Figure 5.7 Main effects plot for P (pressure) and T (temperature) obtained from Minitab17 for (a) Sulfur Conversion, (b) Bed Deposition

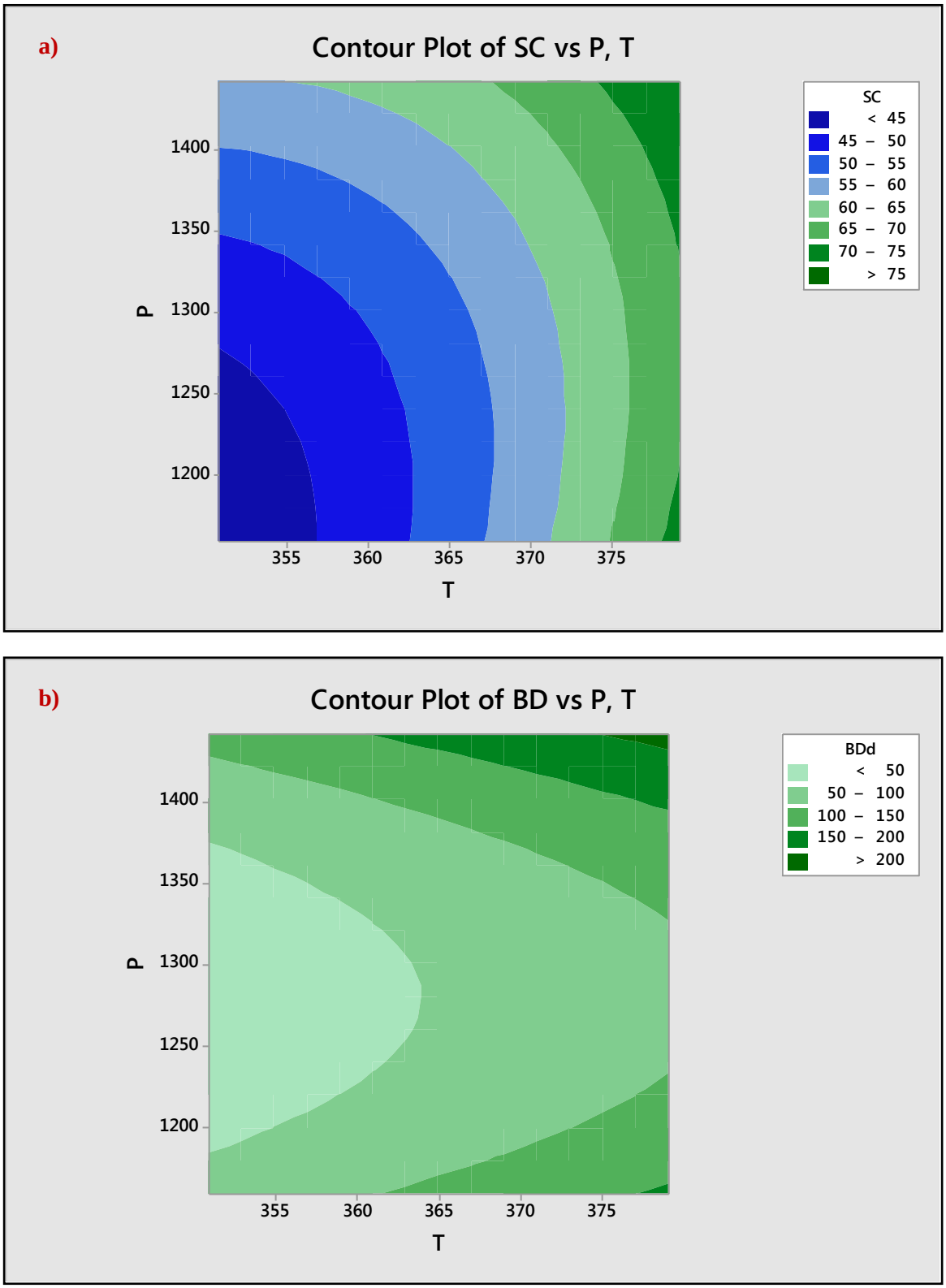


Figure 5.8 Contour plot for P (pressure) and T (temperature), obtained from Minitab17 for (a) Sulfur Conversion, (b) Bed Deposition

Kaolin	Asphaltene coated kaolin
1.Less deposition on reactor assembly	1.Maximum deposition on reactor assembly
2.Most fines in the oil or on catalyst bed	2.Most fines in the oil
3.Higher catalytic activity	3.Lower catalytic activity
4.More deposits on the top screen of the catalyst basket	4.More deposits at the bottom and side walls of the reactor vessel
5.Fines did not settle at the bottom of the stirring feed	5.Fines settled at the bottom of the stirring feed
6.High pressure and lower temperature would lead to minimum bed deposition	6.Pressure had a reverse effect on bed deposition in this case

Table 5.8 Comparison between kaolin and asphaltene coated kaolin on catalyst performance

6. Summary and Conclusions

6.1 Summary

In this work, the impact of hydrotreating process parameters on the deposition of fine particles that are present in bitumen-derived light gas oil was studied. The impacts of various process conditions on kaolin deposition and asphaltene coated kaolin deposition on the hydrotreating catalyst were separately studied.

For kaolin spiked LGO feed (Phase 1):

- The study and analysis of results suggest that the major problem due to fine particle deposition is not the immediate deterioration in the catalyst activity (hydrodesulfurization), but the deposition of these fines on the catalyst bed, which leads to pressure drop in the reactor. However, when the fines deposition builds up on the catalyst bed, it might lead to catalyst fouling which consequently would result in poor catalyst activity at later stages.

- The textural properties of the catalyst do not change due to fines deposition as the model fine particles (6-7 μm) are larger than the pore size (8 nm) of the mesoporous catalyst. The fines do not enter the pores of the catalyst and hence unless there is clogging in the catalyst bed, the catalytic activity is not affected greatly by the initial deposition of fines. This could be the reason that there is not drastic fall in the sulfur conversion due to fines deposition.

- Out of the tested process parameters for fines deposition, temperature was found to be the most dominating; where, higher temperature led to higher bed deposition. At higher temperature (375 °C) individual impact of temperature as process parameter over-shadows the pressure. However, when particle loading (1, 1.25 and 1.5 g) and pressure (1200, 1300 and 1400 psig) are varied with temperature (355, 365 and 375 °C), the combined effects of P*T and the individual impact of PL (particle loading) dominate; as seen from the statistical analysis as well as from the individual effect of the temperature study.

- Models for the deposition of fine particles on the catalyst bed and sulfur conversion for the feed were developed. The optimization study for phase 1 revealed that if the particle loading of the feed was increased from 800 mg to 1600 mg / 200 ml of LGO, lowering the temperature and increasing the pressure would yield less bed deposition (100 mg). This optimization would not affect the HDS activity of the catalyst but reduce the probable increase in bed deposition for a high particle loading feed.

For asphaltene coated kaolin spiked feed (Phase 2)-

- The size of the fine particles certainly impacts the bed deposition. Small-sized model fines (4-6 μm) led to higher (62.6% loading) bed deposition at 375 °C; whereas large-sized particles led to less (36.9% loading) deposition of fines on the bed at the same reaction conditions. Perhaps, the smaller sized particles were easily passed through the mesh of the catalyst basket during the hydrotreating runs.

- Temperature clearly stands as a dominating parameter as compared to pressure; when particle loading in the feed is maintained constant. The individual impact of temperature is so dominant that the trend of increase in bed deposition with an increase in temperature is observed in main effects plot as well as individual parameter study. However, unlike in case of kaolin spiked feed, the combined effect of pressure and temperature on bed deposition is not seen in case of asphaltene coated kaolin spiked feed. As, the model for bed deposition (BD) does not have P*T term.

- The deposition trends in different zones within the catalyst basket were analyzed quantitatively using XRF and the results were supported by SEM images as well. There was a tendency for more fines deposition towards the bottom of the catalyst bed packed in the basket in Phase 2. Thus, asphaltene coated kaolin led to deep-bed depostion.

- The regeneration study showed that there is chemical interaction between the deposited fines and the hydrotreating catalyst. This caused the surface removal of deposited fines but some fines were still present and the catalytic activity after regeneration did not increase. This is further supported by FTIR plot that suggests the

formation of Si-C-Si bond. Si of alumino silicates interacts with carbon formed during the course of reaction and gets deposited on the catalyst particle. Thus, reducing its activity.

- The thermal effect study shows that there is no particle deposition on the catalyst bed in the absence of the hydrotreating catalyst; even when the fines entrained feed is treated at the same conditions (1300 psig and 365 °C). The effect of time on particle deposition was also studied and it was found that bed deposition increases with an increase in reaction time. As the fines get more time to interact with the catalyst, 8 h reaction gave maximum bed deposition when compared to 3 and 5 h at same process conditions (1300 psig and 365 °C).

6.2 Conclusions

The following conclusion are drawn from this research-
For kaolin spiked LGO feed (Phase 1):

- The textural properties of the catalyst are not affected by kaolin deposition.

- The variation in the fine particle loading did not affect the sulfur conversion of the kaolin spiked feed.

- FT-IR spectroscopy study suggests an interaction between catalyst and the kaolin particles.

- High reaction temperature led to more particle deposition on the catalyst as seen in the SEM images and main effects plot. However, main effects plot for sulphur conversion clearly show that higher temperature gives higher conversion. Thus, optimization is relevant for the study.

- Optimization results suggest that for a feed with higher fine particles loading (1500 mg), low temperature (360°C) and higher pressure (1450 psi) can help in decreasing the bed deposition without affecting the sulfur conversion of the feed.

For asphaltene coated kaolin spiked feed (Phase 2)-

- Both temperature and pressure impact the deposition of model fines. The bed deposition increases with an increase in temperature. However, the trend is difficult to predict with pressure variation.

- Large particle size of the model fines led to less bed deposition.

- When asphaltene coated kaolin is used as model fines, more fines get deposited on the reactor assembly, as seen from the mass balance studies.

- Results for cake filtration and deep filtration on the catalyst bed showed that asphaltene coated kaolin led to deep-bed deposition.

- Regeneration studies show that the deposition of fines on the catalyst is a surface adsorption process. It does not chemically impact the catalytic activity.

Thus, it can be inferred that this study addresses the impact of process variables on the fine particle deposition on the catalyst bed. These findings might help to set the operating conditions for the hydrotreaters in such a way as to reduce fines deposition without deteriorating the catalyst activity.

6.3 Recommendations

- The optimized process parameters can be further scaled up to a trickle-bed reactor in the laboratory to get precise results that can be closely related to the industrial reactor.

- The interaction between the catalyst and the fines can be further studied in detail with the help of X-Ray Absorption Spectroscopy (XAS). This might give an insight as to what element of the catalyst interacts with the fines and in which chemical state.

- In-situ study for the deposition trends of fines in the trickle-beds can be another useful dimension to this work.

7. References

Badoga S., Dalai A.K., Adjaye J., Hu Y. "Combined Effects of EDTA and Heteroatoms (Ti , Zr , and Al) on Catalytic Activity of SBA-15 Supported NiMo Catalyst for Hydrotreating of Heavy Gas Oil." Industrial & Engineering Chemistry Research 53, 2137–2156 (2014).

Botchwey C., Dalai A.K., Adjaye J. "Two-Stage Hydrotreating of Athabasca Heavy Gas Oil with Interstage Hydrogen Sulfide Removal : Effect of Process Conditions and Kinetic Analyses." Industrial and Engineering Chemistry Research 43, 5854–5861 (2004).

Choo C., Tien C."Analysis of the Transient Behavior of Deep-Bed Filtration" Journal of Colloid and Interface Science 169, 13–33 (1995)

Chowdiah P., Wasan D.T., Gidaspow D."Electrokinetic Phenomena in the Filtration of Colloidal Particles Suspended in Nonaqueous Media." AIChE Journal 27(6), 975–984 (1981).

Coulier, L., Beer V. H., van Veen J., Niemantsverdriet J. W. "Correlation between Hydrodesulfurization Activity and Order of Ni and Mo Sulfidation in Planar Silica-Supported NiMo Catalysts: The Influence of Chelating Agents." Journal of Catalysis 197(1), 26–33 (2001).

Dehkissia S., Bac A., Iliuta I., Larachi F. "Dynamics of Fines Deposition in an Alternating Semifluidized Bed." AIChE Journal 54(8), (2008).

Dunbar, R. B. 2009. Canada's Oil Sands - A World-Scale Hydrocarbon Resource.

EIA. 2016. "Energy Information Administration." (October). Retrieved (https://www.eia.gov/forecasts/steo/report/global_oil.cfm).

Ferdous D., Bakhshi N.N., Dalai A.K., Adjaye J. "Synthesis, Characterization and Performance of NiMo Catalysts Supported on Titania Modified Alumina for the Hydroprocessing of Different Gas Oils Derived from Athabasca Bitumen." Applied Catalysis B: Environmental 72, 118–128 (2007)

Ferdous D., Dalai A.K., Adjaye J. “A Series of NiMo/Al2O3 Catalysts Containing Boron and Phosphorus.” Applied Catalysis A: General 260(2), 153–162 (2004 a).

Ferdous D., Dalai A.K., Adjaye J. 2004b. “A Series of NiMo/Al2O3 Catalysts Containing Boron and Phosphorus.” Applied Catalysis A: General 260(2), 137–151 (2004 b)

Gawel I., Bociarska D., Biskupski P. “Effect of Asphaltenes on Hydroprocessing of Heavy Oils and Residua.” Applied Catalysis A: General 295(1), 89–94 (2005).

Giesy J. P., Anderson J.C., Wiseman S.B. “Alberta Oil Sands Development.” Proceedings of the National Academy of Sciences of the United States of America 107(3), 951–952 (2010).

Gray M. R., Srinivasan N., Masliyah J.H.“Pressure Buildup in Gas-Liquid Flow through Packed Beds due to Deposition of Fine Particles.” Canadian Journal of Chemical Engg. 80(June), 346–354 (2002).

Grill A. “Porous pSiCOH Ultralow- K Dielectrics for Chip Interconnects Prepared by PECVD.” Annual Review of Materials Research 39(1), 49–69 (2009).

Gruesbeck C. “Entrainment and Deposition of Fine Particles in Porous Media.” Society of Chemical Engineering 22(06), 847–856 (1982).

Haraguchi L., Loh W., Mohamed R. S. “Interfacial and Colloidal Behavior of Asphaltenes Obtained from Brazilian Crude Oils.” 32, 201–216 (2001).

Iliuta I., Larachi F. “Fines Deposition Dynamics in Packed-Bed Bubble Reactors.” Industrail Engineering Chemistry Research 42, 2441–2449 (2003).

Iliuta I., Larachi F., Bernard P. “Fines Deposition Dynamics in Gas–liquid Trickle-Flow Reactors.” AIChE Journal 49(2), 485–495 (2003).

Kang K., Azargohar R., Dalai A.K., Wang H. “Noncatalytic Gasification of Lignin in Supercritical Water Using a Batch Reactor for Hydrogen Production: An Experimental and Modeling Study.” Energy & Fuels 29(3), 1776–1784 (2015).

Kotlyar L. S., Sparks B. D., Woods J. R., Chung K.H. “Solids Associated with the Asphaltene Fraction of Oil Sands Bitumen.” Energy & Fuels 13(2), 346–350 (1999 a).

Kotlyar L. S., Sparks B. D., Woods J. R., Chung K. H. “Solids Associated with the Asphaltene Fraction of Oil Sands Bitumen.” 346–350 (1999 b).

Leffler, William. 2000. Petroleum Refining in Nontechnical Language. 3rd Editio. PennWell Corporation.

Liu, J., Xu Z., Masliyah J. “Interaction between Bitumen and Fines in Oil Sands Extraction System: Implication to Bitumen Recovery.” *Canadian Journal of Chemical Engg.* 82, 655–666 (2003).

Liu, J., Xu Z., Masliyah J. “Processability of Oil Sand Ores in Alberta.” *American Chemical Society* 19(5), 2056–2063 (2005).

Selucky M. L., Chu Y., Ruo T., Strausz O. P. “Chemical Composition of Athabasca Bitumen.” Fuel 56(October), 369–381 (1977).

Elimelech M, O’Melia C. R. “Effect of Particle Size on Collision Efficiency in the Deposition of Brownian Particles with Electrostatic Energy Barriers.” Energy & Fuels 6(6), 1153–1163 (1990).

Cruz M., José L. “Study of Monolayer to Multilayer Adsorption of Asphaltenes on Reservoir Rock Minerals.” Colloids and Surfaces A: Physicochemical and Engineering Aspects 340(1-3), 149–154 (2009).

Mgbemena C. O., Ibekwe O. N., Sukumar R., Menon R. “Characterization of Kaolin Intercalates of Oleochemicals Derived from Rubber Seed (Hevea Brasiliensis) and Tea Seed (Camelia Sinensis) Oils.” Journal of King Saud University - Science 25(2), 149–155 (2013).

Murgich J. “Intermolecular Forces in Aggregates of Asphaltenes and Resins.” Petroleum Science and Technology 20(9-10), 983–997 (2002).

Narayan R., Coury R., Masliyah J. H., Gray M. “Particle Capture and Plugging in Packed-Bed

Reactors.” *Ind.Eng. Chem. Res* 36(No. 11), 4620–4627 (1997 a).

Narayan R., Coury R., Masliyah J. H., Gray M. R. “Particle Capture and Plugging in Packed-Bed Reactors.” American Chemical Society 36(1976), 4620–4627 (1997 b).

Hossein N., Kariznovi M., Abedi J. “Physical Properties and Extraction Measurements for the Athabasca Bitumen + Light Hydrocarbon System : Evaluation of the Pressure Effect , Solvent-to-Bitumen Ratio , and Solvent Type.” Journal of Chemical & Engineering Data 56, 4261–4267 (2011).

Palcheva R., Kaluza L., Spojakina A., Tyuliev G. “NiMo/γ-Al2O3 Catalysts from Ni Heteropolyoxomolybdate and Effect of Alumina Modification by B, Co, or Ni.” Chinese Journal of Catalysis 33(6), 952–961 (2012).

Stelmack P., Masliyah J. H., Czarnecki J., Gray M. R. “Particle Deposition from Non-Aqueous Suspensions in an Impinging Jet.” 403 (1999).

Rana M. S., Sámano V., Ancheyta J., Diaz J. “A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua.” Fuel 86(9), 1216–1231 (2007).

Ranade. 2011. *Trickle Bed Reactors*. Spain: Elsevier B.V.

Saikia, N. “Characterization, Beneficiation and Utilization of a Kaolinite Clay from Assam, India.” Applied Clay Science 24, 93–103 (2003).

Santen V., Neurock M. “Concepts in Theoretical Heterogeneous Catalytic Reactivity.” Catalysis Review 37(4), 557–698 (2006).

Satterfield, C. N. “Heterogeneous Catalysis in Industrial Practice, Charles N. Satterfield, 2nd E.” (1996)

Sparks B., Kotlyar L., O’Carroll J., Chung K. “Athabasca Oil Sands: Effect of Organic Coated Solids on Bitumen Recovery and Quality.” Journal of Petroleum Science and Engineering 39(3-4), 417–430 (2003).

Strausz O. P. “Chemical Composition of Athabasca Bitumen: The Saturate Fraction.” Energy & Fuels 24(9), 5053–5072 (2010).

Strausz O. P. “Chemical Composition of Athabasca Bitumen : The Distillable Aromatic Fraction.” Energy & Fuels 25, 4552–4579 (2011).

Vaezi G., Farid R., Sanders S., Masliyah J. H. “Flocculation Kinetics and Aggregate Structure of Kaolinite Mixtures in Laminar Tube Flow.” Journal of Colloid and Interface Science 355(1), 96–105 (2011).

Wang, S. 2000. “Chemistry of Fine Particlesin Hydrotreator Reactor.” University of Alberta.

Wang S., Chung K., Gray M. R. “Role of Hydrotreating Products in Deposition of Fine Particles in Reactors.” Fuel 80(2001), 1079–1085 (2001).

Wang S., Chung K. H., Masliyah J. H., Gray M. R. “Deposition of Fine Particles in Packed Beds at Hydrotreating Conditions : Role of Surface Chemistry.” Industrial & Engineering Chemistry Research 38, 4878–4888 (1999).

Yu C., Ramanathan S., Oyama S. “New Catalysts for Hydroprocessing : Bimetallic Oxynitrides M I – M II – O – N (M I , M II = Mo , W , V , Nb , Cr , Mn , and Co).” Journal of Catalysis 173, 1–9 (1998).

Zhao S. “A Benchmark Assessment of Residues : Comparison of Athabasca Bitumen with Conventional and Heavy Crudes.” Fuel 81, 737–746 (2002).

8. Appendices

Appendix A

Table A.1 Carbon content and particle size analysis of kaolin, asphaltene and prepared fines

Sample name	**Carbon content (wt%)**	**Size range (µm)**
Kaolin 1	00.13	6-7
Kaolin 2	00.08	2-3
Asphaltene	80.00	-
Fines from kaolin 1	3	9-11
Fines from kaolin 2	5	4-6

Table A.2 Typical mass balance for phase 1

Exp No.	Total fines spiked in 200 ml LGO feed (mg)	Bed deposition (±5 mg)	Fines in 200 ml oil (±5 mg)	Reactor assembly deposition (±5 mg)
1	1250	247.8	679.6	322.6
2	1250	278.9	622.4	348.7
3	1250	287.4	599.0	363.6
4	1670	479.1	712.3	478.6
5	1500	307.8	694.6	497.6
6	1250	293.1	522.4	434.5
7	1250	251.7	566.3	432.0
8	1000	220.5	481.9	297.6
9	830	46.1	397.5	386.4
10	1250	157.8	601.9	490.3
11	1000	189.9	518.4	291.7
12	1250	288.0	508.4	453.6
13	1250	289.6	513.4	447.0
14	1250	276.2	489.1	484.7
15	1500	383.3	597.1	519.6
16	1250	281.0	531.4	437.6
17	1500	598.2	499.6	402.2
18	1500	247.8	708.5	543.7
19	1000	278.9	437.8	283.3
20	1000	287.4	399.0	313.6

Table A.3 Typical mass balance for phase 2

Exp No.	Total fines spiked in 200 ml LGO feed (mg)	Bed deposition (±5 mg)	Fines in 200 ml oil (±5 mg)	Reactor assembly deposition (±5 mg)
1	1000	64.8	245.9	689.3
2	1000	132.7	301.0	566.3
3	1000	135.1	375.2	489.7
4	1000	42.3	430.5	527.2
5	1000	57.8	426.1	516.1
6	1000	54.8	356.9	588.3
7	1000	54.8	431.5	513.7
8	1000	111.7	419.1	469.2
9	1000	54.8	419.1	526.1
10	1000	54.8	401.5	543.7
11	1000	27.7	379.2	593.1
12	1000	54.8	432.4	512.8
13	1000	139.6	356.6	503.8

Appendix B

Figure B.1 Photograph of the glass beads without black (fines) deposit in the absence of NiMo/γAl_2O_3 catalyst.

Figure B.2 Photograph of the glass beads with black (fines) deposit in the presence of NiMo/γAl_2O_3 catalyst.